On the Thermal Cycloisomerization of Long-Chain Alkylacetylenes in the Gas Phase

Bernd Ondruschka[a], Gerhard Zimmermann*[a], Matthias Remmler[a], Ulrich Ziegler[a], Frank-Dieter Kopinke[a], Bernhard Olk[b], and Matthias Findeisen[b]

Central Institute of Organic Chemistry, Department for Basic Organic Materials[a]
Central Institute of Isotope and Radiation Research[b]
G. D. R. Academy of Sciences,
Leipzig-7050, DDR

Received September 26, 1988 (Revised Manuscript Received December 19, 1988)

Keywords: Alkyne / Carbene / Cycloisomerization / Pyrolysis

The thermal cycloisomerization of some alkylacetylenes was investigated in a tubular quartz reactor. At 570°C 1-hexyne (**1**) rearranges to 3-methyl-1-cyclopentene (**5**) with a selectivity of about 27 by a reaction sequence including an acetylene-vinylidene rearrangement and 1,5-C,H insertion of the intermediately formed alkylidenecarbene species. 5-methyl-1-hexyne (**2**) behaves analogously forming 3,3-dimethyl-1-cyclopentene (**6**), while 2-hexyne (**3**) provides 1-methyl-1-cyclopentene (**7**) indicating that the acetylene-vinylidene rearrangement is obviously not restricted to 1,2-H shifts. The mechanism of the cycloisomerization of alkylacetylenes is investigated by means of D-labeled parent alkynes. The results show that the unimolecular cycloisomerization via alkylidenecarbenes obviously can be an important channel despite the dominance of a radical chain course.

Über die thermische Cycloisomerisierung langkettiger Alkylacetylene in der Gasphase

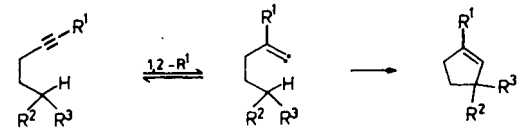
Die thermische Cycloisomerisierung einiger Alkylacetylene wurde in einem Laborrohrreaktor aus Quarzglas untersucht. 1-Hexin (**1**) wird dabei durch 1,2-H-Verschiebung und 1,5-C,H-Insertion des intermediär gebildeten Pentylidencarbens (vgl. Schema 1) in 3-Methyl-1-cyclopenten (**5**) umgelagert. 5-Methyl-1-hexin (**2**) reagiert analog; es entsteht 3,3-Dimethyl-1-cyclopenten (**6**). Im Gegensatz zur Bildung von in 3-Stellung methylierten Cyclopentenen aus 1-Alkinen ensteht aus 2-Hexin (**3**) 1-Methyl-1-cyclopenten (**7**). Offenbar ist die Acetylen-Vinyliden-Umlagerung nicht auf 1,2-H-Verschiebung beschränkt. Der Mechanismus der Cycloisomerisierung von Alkylacetylenen wird durch Untersuchungen mit D-markierten Alkinen bestätigt. Die Ergebnisse lassen den Schluß zu, daß die Cycloisomerisierung ohne weiteres mit dem überwiegend nach einem Radikalketten-Mechanismus verlaufenden thermischen Zerfall konkurrieren kann.

Very recently we have studied the gas-phase pyrolysis of alkylacetylenes $\geq C_5$ at 500 to 600°C[1] (see also ref.[2,3]). Whilst the cracked gases formed are obviously a result of radical chain processes the origin of essential parts of the cracked liquids is somewhat mysterious. Particularly surprising is the formation of hydrocarbons with cyclopentene structures, which in each case are isomeric to the corresponding parent alkynes. One might expect that the formation of cyclopentenes should happen by internal addition of alkenyl radicals known to give five-membered ring species (see, for example, ref.[1]). If radical pathways are involved appropriate product mixtures would have been expected, but the results described in ref.[1] illustrate that the products in question seem to consist essentially of one compound only.

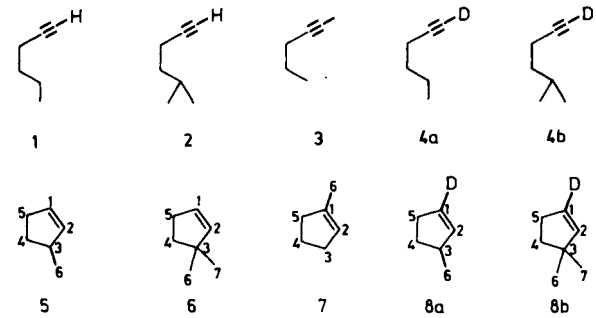
Quite recently we have observed that the formation of five-membered ring hydrocarbons from alkynes $> C_5$ does not require bimolecular reaction steps as are necessary for radical cyclizations[1]. These results[4,5] suggested that the cycloisomeres originate by acetylene-vinylidene rearrangements[6] followed by cyclization of the vinylidene species by 1,5-C,H insertion (Scheme 1).

Within the scope of our investigations on the thermal cyclization and aromatization of highly unsaturated hydrocarbons (see, for example ref.[7–9]) we have now made a more thorough study of the composition of the cycloisomers formed from 1-hexyne (**1**), 5-methyl-1-hexyne (**2**), 2-hexyne (**3**), [1-D_1]-1-hexyne (**4a**) and [1-D_1]-5-methyl-1-hexyne (**4b**) (Scheme 2) as well as the mechanism of their cycloisomerization.

Scheme 1



Scheme 2



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Pyrolysis of 1-Hexyne (1) and [1-D_1]-1-Hexyne (4a)

On pyrolyzing **1** at 560°C (6 s, flow system, molar ratio Ar:**1** ≈4, conversion of **1** ca. 30%) 3-methyl-1-cyclopentene (**5**) is an important constituent of the cracked liquid, but it is formed with a selectivity[10] of 12 only[1]. To facilitate the cycloisomerization of **1** to **5** we decided to optimize the gas-phase pyrolysis with respect to maximum yields of **5**.

By systematic variation of the reaction temperature (T = 500 to 600°C) and the residence time in the hot section (τ = 3–12 s) at a constant molar ratio of the diluent used (Ar) and **1** (≈4) we found a significant dependence of the selectivity of **5** on these parameters (Figure 1). Maximum selectivities are thus to be expected at about 560°C and τ less than 3 s[11]. Additionally, we found that at 570°C but for 1.5 s only and a higher molar ratio of Ar:**1** (≈5.5) **1** isomerizes to **5** with a selectivity of even 27 in the course of which about 20% of **1** is converted. Under similar conditions the yield of the condensed total liquid amounted to somewhat more than 86% of the original **1**. The result of capillary GC analysis of the cracked liquid compounds (sum after deduction of unconverted **1**) is given in Table 1. It clearly illustrates that the cracked liquid nearly exclusively consists of cyclic C_5/C_6 hydrocarbons.

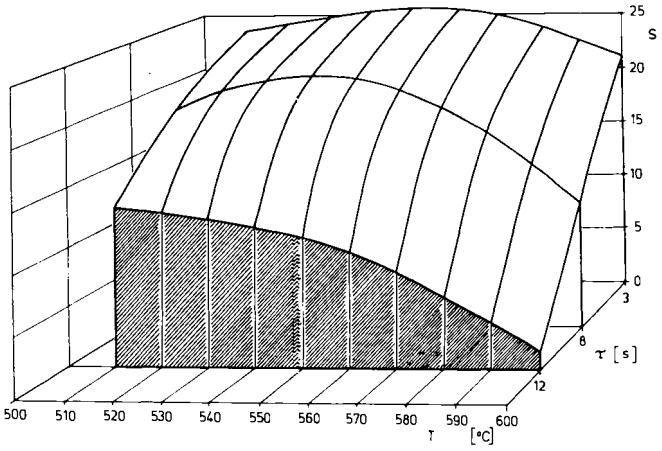


Figure 1. Pyrolysis of 1-hexyne (**1**). Dependence of selectivity S on reaction temperature T and residue time τ in the hot section

Table 1. Composition of the liquid product mixture from **1**–**3** (S values, T = 570°C, τ = 2 s)

Products	**1**	**2**	**3**
Cyclopentadiene	< 1	1	< 1
1-Pentene-3-yne	–	–	14
Pentadienes (Σ)	2	–	2
Hexadienes (Σ)	–	1	–
Methylcyclopentadienes	5	10	3
Methylenecyclopentenes	< 1	< 1	< 1
1-Methyl-1-cyclopentene (**7**)	–	–	17
3-Methyl-1-cyclopentene (**5**)	27	–	–
3,3-Dimethyl-1-cyclopentene (**6**)	–	26	–
Cyclohexene	3	–	–
C_7H_{12}	–	4	–
Vinyl- and ethylidenepentane	< 1	–	–
Benzene	1	1	1
Toluene	< 1	< 1	–
Others	2	2	1

Side products are pentadiene isomers, methylenecyclopentenes, vinyl- and ethylidenecyclopentane, and toluene as well as higher aromatics. 4-Methyl-1-cyclopentene, methylenecyclopentane, dimethylcyclopentadienes (C_7H_{10}), and dimethylcyclopentenes (C_7H_{12}) in this fraction could not be detected by means of the efficient GC technique used. To check these results in another way unconverted **1** and its isomer **5** were separated in small amounts by preparative GC and analyzed by ^{1}H and ^{13}C NMR. The comparison of the corresponding spectral data with those of authentic **1** and **5**[12] leave no doubt that the separated products are of pure spectral quality. In analogous experiments with [1-D_1]-1-hexyne (**4a**)[13] we succeeded in separating [1-D_1]-3-methylcyclopentene (**8a**) by comparing its spectral data with those of the undeuterated hydrocarbon of **5** (see Experimental Part).

Pyrolysis of 5-Methyl-1-hexyne (2) and [1-D_1]-5-Methyl-1-hexyne (4b)

The acetylenes **2** and **4b** were synthesized and characterized as described in the Experimental Part. The thermal conversion as well as the procedure of the product separation and analysis were performed as in the case of **1**. The yields arising from the two parent alkynes were found to be similar for comparable pyrolysis conditions, reaching a maximum selectivity of about 26 [565°C, 1.5 s, Ar:**2** (**4b**) ≈6] at a conversion of nearly 25%. In this case the cracked liquid essentially consists of cyclic C_6/C_7 hydrocarbons (Table 1). Hexadienes and methylenecyclopentenes, benzene, toluene, and higher aromatics with a selectivity <1 were detected as side products. As for **1** we separated the unconverted parent alkynes (**2** and **4b**) as well as the cycloisomers **6** and **8b**, respectively, by preparative GC and recorded their ^{1}H- and ^{13}C-NMR spectra. In the NMR spectra of cycloisomers obtained from **2** and **4b** no signals could be established besides those belonging to **6** and **8b**, respectively. In **8b** the position of the D atom at C-1 could be made evident by means of homonuclear ^{1}H-NMR decoupling experiments[12]. Selective decoupling of the protons at C-4 (t at δ = 1.57, ^3J = 7.4 Hz) gives a doublet at C-5 (δ = 2.27, ^4J = 2.2 Hz). Analogous decoupling of the protons at C-5 results in a singlet for C-4 (δ = 1.57). The structure is confirmed by ^{13}C-NMR spectroscopy: a triplet for C-1 at δ = 127.6 ($J_{C,D}$ = 25 Hz) and a low-field shifted doublet for C-2 at δ = 141.7 ($J_{C,H}$ = 158 Hz) as to be expected for **8b**.

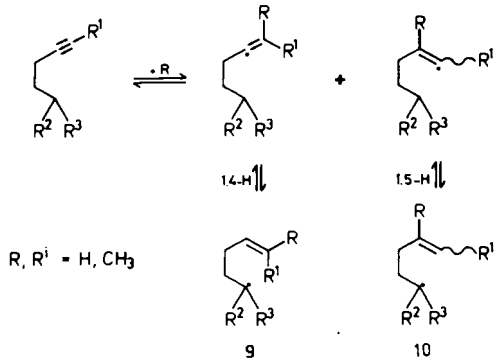
Pyrolysis of 2-Hexyne (3)

Hydrocarbon **3** was pyrolyzed at 570°C (2 s, Ar:**3** ≈6) as described for **1**. After cooling and separating the cracked gases the liquid fraction was analyzed by capillary GC. The liquid products formed from **3** are listed in Table 1. In agreement with the results given in ref.[1] there are two main products: 1-pentene-3-yne and a product whose GC retention time behaves exactly like that of authentic **7**. Consequently, we assigned to it the structure of 1-methyl-1-cyclopentene. Additionally, small amounts could also be separated by means of preparative GC. The ^{1}H-NMR and MS data coincide completely with the data described for **7** in ref.[12].

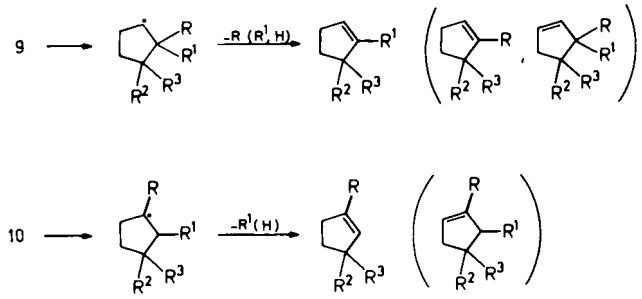
Discussion

There is no doubt that the majority of products formed on pyrolyzing long-chain alkynes $\geq C_5$ originates from a radical chain process[1]. Contradicting such mechanism seems to be at least the formation of cycloisomers from the respective parent alkynes, represented by **5** (from **1**), **6** (from **2**), **7** (from **3**), **8a** and **8b** (from **4a** and **4b**, resp.). In principle, the formation of alkylcyclopentenes should be possible as a result of radical processes[1]. At 500–600°C the addition of β-radicals[14] to C≡C triple bonds is certainly possible (Scheme 3). From the resulting vinyl-type radicals[15] alkenyl radicals (**9**, **10**) could be formed by 1,4- and 1,5-H radical isomerization[16] which are evidently capable of endo- and exocyclization[17] (Scheme 4).

Scheme 3



Scheme 4

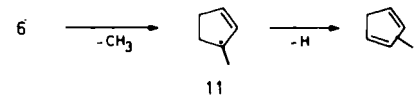


From radical **9** (R = R¹ = R² = H; R³ = CH₃) as well as from **10** (R = R¹ = R² = H; R³ = CH₃) the formation of a 1:1 mixture of **5** and 4-methyl-1-cyclopentene should be expected, whereas from **10** (R = R³ = CH₃; R¹ = R² = H) a 1:1 mixture of 1,3- and 1,4-dimethyl-1-cyclopentenes should be formed. Experimentally only **5** is formed with S = 27. Though analogous considerations for **2** should lead to a 1:1 mixture of 3,3- and 4,4-dimethyl-1-cyclopentenes as well as to a mixture preferably consisting of 3,3-dimethyl- besides smaller amounts of 2,3,3-trimethyl-1-cyclopentene and a 1:1 mixture of 1,3,3- and 1,4,4-trimethyl-1-cyclopentenes, also in this case **6** was formed exclusively with S = 26. The same is valid for hydrocarbons with cyclopentene structures formed from **3**. Besides methylcyclopentadienes (C_6H_8) **7** could be proved only with S = 17. We regard these results as convincing evidence that under the conditions used there are obviously only small changes for the formation of five-membered ring hydrocarbons by radical steps. Hence we conclude (see also ref.[1]) that the 1,x-H isomerization of vinyl-type to alkenyl radicals cannot play an important role (but see ref.[15–17]) and that in accordance with theory the CH_3 addition to the triple bond is disfavoured relative to H addition (absence of products with one C atom more than respective parent alkynes). Therefore it is obvious that the cycloisomerization of the parent alkynes very probably occurs via alkylidenecarbenes (Scheme 1). Such a view is strenghtened by results described in ref.[1] (see also ref.[18–20]), according to which at 240°C alkylidenecarbenes $\geq C_5$ preferably cyclize by 1,5-C,H insertion to cyclopentenes, as well as by the fact that suitable phenyl-substituted[21,22] (at >700°C) and acylated alkynes (α-alkynones)[23] (at about 600°C) are able to cyclize by a mechanism being thought to occur by a 1,2-H shift (acetylene-vinylidene rearrangement) followed by C–H insertion.

The cyclization of α-alkynones could be attributed to special structural conditions favouring the acetylene-vinylidene rearrangement already at a relative low temperatur range. On the other hand the cyclization of, e.g., aryl-substituted acetylenes seems to require higher temperatures (680 to 790°C, see ref.[24]). In such cases the lack of chances for degradation reactions in radical chains obviously favour the cycloisomerization. In pyrolyzing **1**–**4**, however, the cycloisomerization has to compete with usual radical chain processes. Therefore the maximum selectivities determined for **5**–**8** (S_7 up to 17, other S up to 30) are the results of two competing reaction pathways, the acetylene-vinylidene rearrangement ending in the corresponding cyclopentenes and the radical decompositions, both favoured by increasing temperatures.

It was recently demonstrated[13] that at 240°C 1,5-C,H insertions of alkylidenecarbenes depend strongly on the degree of alkylation at C-5 (1°:2°:3° = 1:54:240). Surprisingly enough, we failed to confirm a similar dependence at temperatures above 500°C: **5** and **6** are formed with nearly the same selectivity. The reason of the disappearence of this influence at higher temperatures has hitherto been largely unknown. One possible qualitative explanation, not experimentally proved as yet, could be the more rapid thermal decomposition of the geminal dimethylated **6** than that of the monomethylated cyclopentene **5**. The C–CH_3 bond cleavage of **6** would afford the methylcyclopentenyl radical **11**, which loses a hydrogen atom to produce methylcyclopentadienes (Scheme 5), found with a selectivity of S = 8 (Table 1).

Scheme 5



From the results discussed so far the most straightforward mechanism of the cycloisomerization of 1-alkynes involves a 1,2-shift of the H atom of the triple bond. To make this

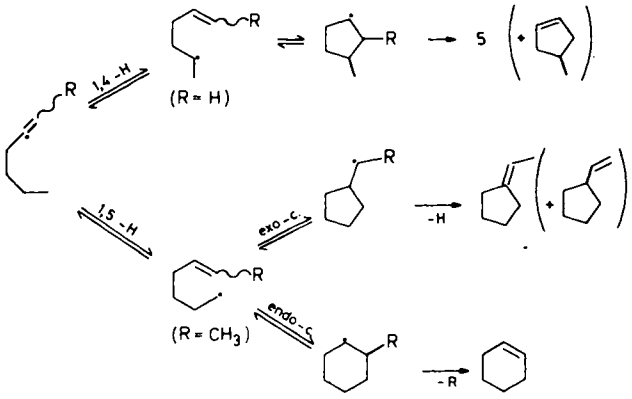
reaction step evident investigations with the D-labeled alkynes **4a** and **4b** were helpful. The cycloisomers formed could be identified as [1-D_1]-3-methyl- **8a** and [1-D_1]-3,3-dimethylcyclopentene **8b** by their spectral data (see Experimental Part). The D-labeling at C-1 confirms the proposed mechanism of the 1-alkyne → 3-alkylcyclopentene isomerization (Scheme 1), and it makes evident that the radical route resulting in [2-D_1]-3-methyl- and [2-D_1]-3,3-dimethylcyclopentene occurs below the spectroscopic detection limit (< 5%), if at all.

In principle the mechanism should not be restricted to 1-alkyne isomerizations. Consequently we suppose that the **3**→**7** isomerization is initiated by an analogous 1,2-CH_3 shift. In contrast to the **1**→**5** and **2**→**6** isomerization, however, the **3**→**7** rearrangement is twofold energetically disfavoured: by the 1,2-CH_3 shift itself and by the necessity of the alkylidenecarbene insertion into the C–H bond of a methyl instead of a methylene or a methyne group. Both handicaps make the **3**→**7** isomerization occur to a lesser extent.

The thermal cycloisomerization reactions described so far emphasize the importance of the 1,5-C,H insertion of alkylidenecarbenes, but the hitherto discussed results do not verify that the cyclization step is exclusively restricted to the 1,5-C,H insertion. Brown et al.[21] have previously reported that arylmethylenecarbenes can undergo 1,6-C,H insertion if there is no way for 1,5-C,H insertion for structural reasons.

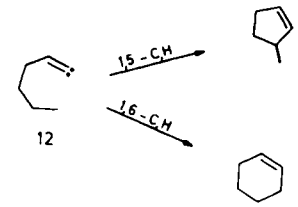
Starting from **1** (or **2**) the 1,6-C,H insertion is possible in principle as an alternative to the 1,5-C,H one, leading to the cyclohexene detected (or C_7H_{12}, possibly 4-methyl-1-cyclohexene). An alternative mechanism of the cyclohexene formation could be a radical process. It requires a β radical addition to the triple bond followed by a 1,5-H isomerization of the intermediate vinyl-type radical, the endocyclyzation of the alkenyl radical[17] and a β(C–C) or β(C–H) scission (see Scheme 6).

Scheme 6



Although the route leading to cyclohexene is the least of the competing pathways depicted in this Scheme[25] cyclohexene is formed to an appreciable extent. Since, however, we failed to detect 4-methyl-1-cyclopentene as well as methylenecyclopentane, and ethylidene- and vinylcyclopentane are only formed to a much lesser extent then cyclohexene, the discussed radical path to cyclohexene should be insignificant. Therefore, the formation of cyclohexene is also thought to occur via a vinylidenecarbene species (pentylidene carbene **12**, Scheme 7). Admittedly, this reaction path is yet rather speculative, but there is no plausible reason against the given interpretation (see also ref.[1]).

Scheme 7



Experimental

NMR spectra: Bruker AM 250, ^{1}H NMR (250 MHz) internal standard HMDSO, in $CDCl_3$; ^{13}C NMR (62.9 MHz) internal standard TMS, in $CDCl_3$. – Gas chromatography: Giede 21.3 (analytical on packed columns), Varian 1740 (capillary GC), self-made set-up based on a Chromatron GCHF 18.3. (6-m stainless-steel column, SE-30, 50–100°C, preparative). – GC-MS: Hewlett Packard system 5985 (20-m glass capillary, methylsilicon oil OV-1, FID, He). – Mass spectra: CH 6 Varian MAT (70 eV).

Preparation of the Parent Alkynes

1-Hexyne (**1**) *and 5-Methyl-1-hexyne* (**2**) were prepared by reaction of sodium acetylide with *n*-butyl and isoamyl bromide, resp., in liquid ammonia (–60°C) as described in ref.[26]. Yields, boiling points and refractivities agreed with the data published (**1**: b.p. 71.5°C, n_D^{20} = 1.3994, GC purity 99%; **2**: b.p. 91°C, n_D^{20} = 1.4052, GC purity 98.5%).

2-Hexyne (**3**) was synthesized and separated according to ref.[27] by reaction of the sodium salt of 1-pentyne with methyl iodide (b.p. 84.5°C, n_D^{20} = 1.4135, GC purity 98.8%).

[1-D_1]-1-Hexyne (**4a**) was obtained by treatment of the sodium salt of **1** with D_2O in dibutyl ether as described in ref.[27]. The D content (98.8%) was determined by MS, the D position at C-1 by ^{1}H NMR. The GC purity amounted to 99.1%.

[1-D_1]-5-Methyl-1-hexyne (**4b**) was prepared from **2** by a three times repeated H-D exchange with alkaline D_2O. The D content was >98.5%. The D position at C-1 was confirmed by ^{1}H-NMR spectral data[13], GC purity amounted to 99.1%.

Preparation of Authentic Cyclopentenes

1-Methyl-1-cyclopentene (**7**): The synthesis was performed as described for the preparation of cyclohexene from cyclohexanol by means of phosphoric acid[28]. 50 g (0.50 mmol) of 1-methylcyclopentanol yielded 45.1 g (0.45 mol) of **7** (after distillative purification). B.p. 75.5°C, n_D^{20} = 1.4319, GC purity 99.1%, impurity methylenecyclopentane.

3-Methyl-1-cyclopentene (**5**) was prepared by reaction of 3-chloro-1-cyclopentene with methylmagnesium iodide in ether following ref.[29] (b.p. 64.8°C, n_D^{20} = 1.4206).

Gas-Phase Pyrolysis: The pyrolysis system used in all runs is described in ref.[1]. It consists of a tubular reactor (V_R ≈ 6.3 ml, length of the quartz tube 50 cm, i.d. 4 mm) connected with a cooling and a separation section. Oxygen-free Ar was used as a diluent in

a molar ratio between 3.5 and 7. The reaction temperature was varied in the range of 500–600 °C, the residence time in the hot section between 1.5 and 12 s and the run time between 30 and 60 min. Behind the reactor outlet the product stream ran through an afterheater (≈160 °C) to keep the product temperature above the dew point for taking overall samples by means of a special sampling technique[30]. Then the product was cooled down and separated into gaseous and liquid products containing the unconverted alkyne as well as the cracked liquid products. C-rich deposits in the reactor were burnt off with air after each run. For selected runs the CO formed was converted into CO_2 be means of a CuO-containing supported catalyst and the CO_2 then determined by titration[31]. In all runs the amount of coke deposited was between 0.3 and 1.2% of the alkyne admitted.

Analyses: Hydrogen and hydrocarbons C_1 to C_4 were analyzed gaschromatographically by means of three different packed columns [(a) 2 m Porapak N, thermal conductivity detector, Ar; (b) 3 m aluminium oxide, thermal conductivity detector, H_2; (c) 9 m oxydipropionitrile on Porasil C, FID, N_2]. The purities of the parent alkynes, the cracked liquid products, and the overall product samples were analyzed by capillary GC (45-m glass capillary, OV-1, 5 min at 25 °C, 4 K min^{-1} to 210 °C, remainders isothermal at 210 °C, FID, N_2). For the quantitative determination of the peak areas an electronic integrator was used (Hewlett-Packard Type 3370 B). The structure assignments to unknown GC peaks were made by comparison of their GC retention time behaviour with those of authentic compounds as well as by comparison of the composition of the fraction before and after catalytic hydrogenation (*n*-pentane, 5 MPa H_2, colloidal Pt). In selected cases the mass spectra from GC-MS (temperatur programmed) were compared with known spectra.

The structures of the products considered to be cycloisomers of **1**–**4** and separated by preparative GC were spectroscopically identified (^{1}H, ^{13}C NMR). All samples were obtained as colorless liquids.

[1-D_1]-3-Methyl-1-cyclopentene (**8a**): ^{1}H-NMR: δ = 5.68–5.75 (m, 1H, 2-H), 2.80–2.83 (m, 1H, 3-H), 2.35–2.46 (m, 2H, 5-H), 2.13–2.21 (m, 1H, 4-H), 1.30–1.46 (m, 1H, 4-H), 1.11 (d, ^3J = 6.9 Hz, 3H, 6-H). – ^{13}C-NMR: δ = 136.6 (d, $J_{C,H}$ = 159 Hz, C-2), 128.6 (t, $J_{C,D}$ = 25 Hz, C-1), 39.9 (d, $J_{C,H}$ = 127 Hz, C-3), 32.0 (t, $J_{C,H}$ = 129 Hz, C-4, -5), 20.8 (q, $J_{C,H}$ = 127 Hz, C-6).

[1-D_1]-3,3-Dimethyl-1-cyclopentene (**8b**): ^{1}H-NMR: δ = 5.43 (t, ^4J = 2.2 Hz, 1H, 2-H), 2.27 (t, d, ^3J = 7.4, ^4J = 2.2 Hz, 2H, 5-H), 1.57 (t, ^3J = 7.4 Hz, 2H, 4-H), 0.98 (s, 6H, 6-H). – ^{13}C-NMR: δ = 141.7 (d, $J_{C,H}$ = 158 Hz, C-2), 127.6 (t, $J_{C,D}$ = 25 Hz, C-1), 45.0 (s, C-3), 38.9 (t, $J_{C,H}$ = 126 Hz, C-4), 31.5 (t, $J_{C,H}$ = 140 Hz, C-5), 28.5 (q, $J_{C,H}$ = 125 Hz, C-6, -7).

3,3-Dimethyl-1-cyclopentene (**6**): The spectral data correspond to those given for the deuterated compound **8b** with two exceptions: ^{1}H-NMR: δ = 5.40–5.45 (m, 2H, 2-H, 1-H). – ^{13}C-NMR: δ = 128.4 (d, $J_{C,H}$ = 155 Hz, C-1).

CAS Registry Numbers

1: 693-02-7 / **2**: 2203-80-7 / **3**: 764-35-2 / **5**: 1120-62-3 / **6**: 58049-91-5 / **7**: 693-89-0 / **8a**: 70104-69-7 / **8b**: 111608-12-9

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