The Preparation of the Last Remaining Acyclic Isomers of Benzene[‡]

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The three acyclic isomers of benzene – 2,3-hexadien-5-yne, 3-methyl-1,2-pentadien-4-yne, and 1,2,3,4-hexatetraene – have been prepared by simple routes from readily available starting materials. The hydrocarbons as well as several side products formed during their synthesis were characterized by their spectroscopic data and typical cycloaddition and isomerization reactions.

Introduction

Structural and functional complexity of chemical compounds depend on the number and type of their constituent atoms. And yet, as shown by the homologous and the vinylogous principle, once a certain degree of complexity has been reached the addition of further atoms often does not lead to principally new properties (functions) any more. Rather, incremental changes are observed when the growth process is continued. In fact, it can be stated that for many classes of compounds from a certain number of atoms on no fundamentally new properties emerge. These considerations may be illustrated for the unsaturated and/or cyclic hydrocarbons with the sum formula C_nH_n. Obviously, the number of combinations that can be generated from the respective carbon and hydrogen atoms increases rapidly with growing n. Counting only hydrocarbons with covalent bonds and maintaining the usual valencies of carbon and hydrogen, that is excluding radicals, carbenes etc., there is no covalent structure for $n = 1$, one for $n = 2$ (acetylene), none for $n = 3$, and 11 for $n = 4$. Now a steep increase sets in and for C_6H_6 not only more than 200 combinations can be constructed – the exact number is 218 – but these demonstrate principles (functions) of fundamental importance for organic chemistry for the first time *in full width*. Clearly benzene, the prototypical *aromatic* hydrocarbon is of greatest importance. But there are other isomers showing other important structural and reactivity concepts: [3]Radialene is the smallest conceivable hydrocarbon consisting of semicyclic double bonds only (*radialenes*) and with [3]prismane the polycyclic *prismane* series begins. The phenomenon of *cross-conjugation* is displayed by benzene isomers such as pentafulvene and 2-ethynyl-1,3-butadiene (see below), whereas *linear conjugation* is demonstrated by hydrocarbons such as 1,3-hexadien-5-yne. Although some electronic features such as *antiaromaticity*, show up first in the C_nH_n series with $n = 4$ already (1,3-cyclobutadiene), they are repeated here (e. g. in 1-vinyl-1,3-cyclobutadiene). Of course, the number of combinations grows further rapidly if one progresses to higher values of n (C_8H_8 allows 7437 combinations, $C_{10}H_{10}$ 369 067[2]), but no additional bonding features of fundamental importance arise. In other words: six carbon and six hydrogen atoms are just enough to generate the various π-systems that are of greatest theoretical and practical value; progressing to higher analogs does not give rise to principally new π-electron patterns.

Returning to the C_6H_6 hydrocarbons, these can be classified into five groups: a) Acyclic (15 isomers), monocyclic (61 isomers), bicyclic (82 isomers), tricyclic (45 isomers), and tetracyclic (15 isomers). Out of these groups only one – the "acyclic isomers of benzene"[3] – consist of compounds that should all be preparatively obtainable under normal laboratory conditions. In all other groups structural features are present that will make the isolation of the respective isomers either impossible or only under very special conditions such as matrix isolation or within the mass spectrometer. These features are inter alia triple bonds in three- to six-membered rings, allene groups in these rings, bridgehead double bonds (violation of Bredt's rule) etc.

The acyclic C_6H_6 isomers are summarized in Scheme 1. Whereas most of these hydrocarbons have been extensively studied – see references[7–19] leading to the pertinent literature – there are three isomers, which have either been mentioned only cursorily in the chemical literature, viz. 2,3-hexadien-5-yne (**8**)[4] or not at all: 3-Methyl-1,2-pentadien-4-yne (**15**) and 1,2,3,4-hexatetraene (**12**). Although we synthesized these three cumulenes nearly 30 years ago, we never published their preparation, the main reason being that we were concentrating our efforts in this area on the

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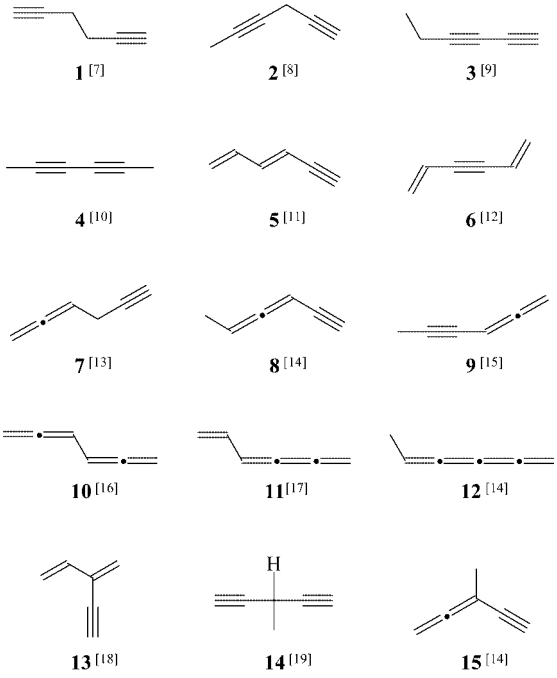
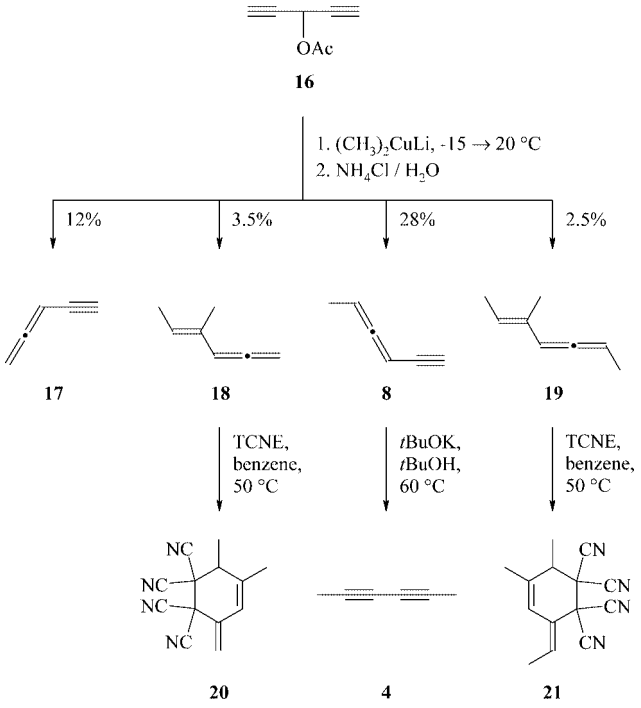
chemical and structural properties of other acyclic benzene isomers such as **7**, **10**, and **13**. However, a recent computational study by Sastry and co-workers on the C_6H_6 potential energy surface aimed at determining the relative stability of the 218 C_6H_6 isomers and their synthetic feasibility[5] prompts us to report our results from 1977.[6] With this publication the preparation of the first class of C_6H_6 isomers is hence complete.



Scheme 1. The acyclic isomers of benzene.

Preparation of 2,3-Hexadien-5-yne (8) and 3-Methyl-1,2-pentadien-4-yne (15)

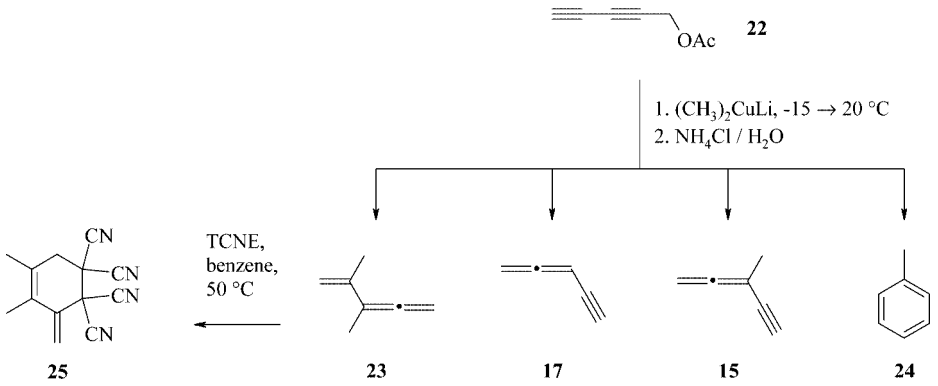
For the preparation of **8** and its branched isomer **15**, we used the alkylation of appropriate propargylacetates with dimethyllithium cuprate first reported by Crabbé and co-workers.[20] Thus 3-acetoxy-1,4-pentadiyne (**16**) was prepared from the corresponding alcohol[21] by treatment with acetyl chloride in pyridine at 0 °C (70% yield). The ester is a colorless liquid which even at –78 °C slowly turns brown and then black. It can, however, be stored in solution at –30 °C indefinitely. For alkylation, **16** was slowly added to a solution of dimethyllithium cuprate in ether at –15 °C. After warming the reaction mixture to room temperature and work-up, the ethereal solution was concentrated and after vacuum transfer (0.01 Torr) separated by preparative gas chromatography. The very complex product mixture showed at least 12 peaks, eight of which, amounting to approximately 10%, were discarded. The structures and yields (isolated yields after gas chromatography) of the four main products are shown in Scheme 2.



Scheme 2. Preparation of 2,3-hexadien-5-yne (**8**).

The first hydrocarbon isolated by preparative gas chromatography was 1,2-pentadien-4-yne (**17**), a known hydrocarbon, which was identified by comparison of its spectroscopic data with those reported in the literature.[22] Next eluted the vinylallene **18** followed by the desired C_6H_6 isomer 2,3-hexadien-5-yne (**8**) as the main product, and readily identified by the spectroscopic and analytical data given in the experimental section. As the most highly alkylated product the vinylallene derivative **19** was finally obtained. To have additional chemical proof for the new hydrocarbons, **18** and **19** were treated in benzene for 6 h at 50 °C with a slight excess of tetracyanoethene (TCNE). After work-up two colorless solids were obtained, which according to ^{1}H NMR analysis (experimental section) have the structures **20** and **21**. When the dienyne **8** was isomerized with potassium *tert*-butoxide in *tert*-butyl alcohol at 60 °C 2,4-hexadiyne (**4**) was obtained as the sole rearrangement product.[10] The base-catalyzed isomerization of allenes and allenynes to alkynes is a well-known phenomenon, which has been observed many times.[23] We assume that in the present case the allenic proton at C-2 is removed first initiating an isomerization of **8** into **9**. Repetition of this process could then lead to **4**.

For the preparation of 3-methyl-1,2-pentadien-4-yne (**15**) the linear acetate **22** was prepared from 2,4-pentadiyn-1-ol[24] with acetyl chloride in pyridine at 0 °C (79% yield). The colorless liquid is much less stable than its branched isomer **16** and decomposes rapidly at room temperature with formation of a black polymeric material. The behavior of **22** during distillation is unpredictable and we have experienced vigorous decompositions with this diacetylene. Methylation of **22** was carried out as described above for **16**, and again a complex mixture of hydrocarbon products



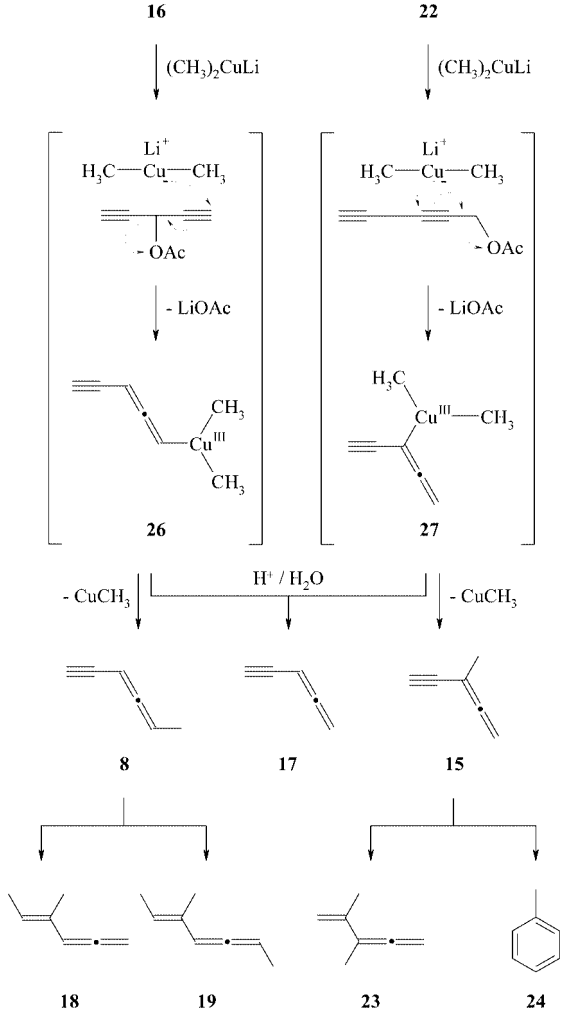
Scheme 3. Preparation of 3-methyl-1,2-pentadien-4-yne (**15**).

was obtained (Scheme 3). The four main products, formed in 1.9:0.7:2.9:1 ratio (GC analysis; yields were not determined quantitatively) could be separated from at least 8 trace components by preparative gas chromatography.

Again, the desired compound **15** was the main component and ethynylallene (**17**) eluting as the second hydrocarbon, was also produced. As the compound with the shortest retention time the vinylallene **23**, a known hydrocarbon,[25] was isolated. Surprisingly, toluene (**24**) was obtained in all experiments, so its formation is evidently not an artefact. The structures of all these compounds follow unambiguously from their spectral and analytical data given in the experimental section. Furthermore, **23** when reacted with TCNE furnished the Diels–Alder adduct **25**, also identified by its spectra.

Although we did not carry out mechanistic experiments the following sequence of steps, based on analogies from the literature,[20] appears reasonable (Scheme 4).

In the first step of the methylation the cuprate reacts with the acetates **16** and **22**, respectively, under propargyl rearrangement to the Cu^{III} intermediates **26** and **27**, while the acetate group is displaced. Methyl transfer and elimination of methyl copper subsequently provides the desired methyl allenes **8** and **15**. On the other hand **26** and **27** are evidently long-lived enough under the reaction conditions to allow hydrolysis to the parent allenyne **17** on work-up. The origin of the other isolated products, the vinyl allenes **18**, **19**, and **23**, and especially toluene (**24**) remains obscure at present. For these higher alkylation products to be generated, methyl groups have to be added to the triple bond of a suitable precursor hydrocarbon. Although a control experiment showed that lithium dimethyl cuprate does not react with 2-penten-5-yne, another experiment with the acetate **16** was revealing. Treating this substrate with the cuprate prepared from one equivalent of copper(I) iodide and *five* equivalents of methyllithium led to a product mixture in which the primary product **8** and the hydrolysis product **17** were not present anymore. Instead **18**, **19** and **24** had been formed in 0.44:4:1 ratio, indicating that allenynes can be alkylated after all. No further experiments were undertaken to shed light on these observations. The formation of aromatic compounds (benzene, toluene) has often been observed in base-catalyzed and thermal isomerizations of acyclic acetylenic and allenic C_6H_6 and C_7H_8 precursors.[26] Since the aromatization process was of no interest here, no effort was undertaken to investigate its mechanism.

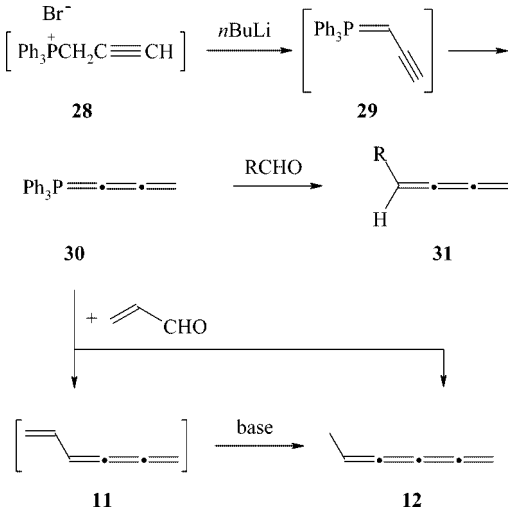


Scheme 4. Mechanisms of formation of 2,3-hexadien-5-yne (**8**) and 3-methyl-1,2-pentadien-4-yne (**15**) and their side products.

Preparation of 1,2,3,4-Hexatetraene (12)

In 1973 Corey and Ruden reported on the stereoselective preparation of *E*- and *Z*-enynes by coupling propargyl tri-

phenylphosphonium bromide (**28**) with a carbonyl component, *n*-butyllithium functioning as the base.[27] In the case of cyclohexane carbaldehyde rather than the expected enyne they isolated cyclohexyl-1,2,3-butatriene and reasoned that the initially generated propargylidenetriphenylphosphorane had undergone a base-catalyzed isomerization to the cumulenic phosphorane **30** prior to the Wittig condensation possibly involving **29** (Scheme 5).



Scheme 5: Generation of 1,2,3,4-hexatetraene (**12**).

If this process could be performed with acrolein it should offer a route to 1,2,3,5-hexatetraene (**11**), a C_6H_6 isomer still unknown at the time when we carried out the experiment, and since then obtained by an alternate protocol.[17] In fact, the Wittig reaction between acrolein and **30** did not lead to **11** but provided its isomer **12** and benzene in trace amounts**.** The highly unstable **12**, it polymerizes rapidly even in solution at –10 °C, was characterized by its NMR and vibrational spectra. In the proton spectrum the methyl group appears as a doublet of triplets (J_1 = 7.5, J_2 = 1.5 Hz) at δ = 1.96 and the remaining protons resonate at 5.17 (unresolved ps-d, J = 7.5 Hz, 2 H, terminal cumulenic H) and 5.71 (m, 1 H, nonterminal cumulenic H). The appearance of the spectrum strikingly resembles that of 1,2-butadiene (methylallene) although the ^5J coupling constant is higher (J = 3.0 Hz) than the value for the ^7J coupling of **12**. The IR spectrum (in CCl_4) with bands at 2070 cm^{-1} (m), 1675 (s), 1610 (s) and 840 (m) support the structure proposal, the aliphatic C,H-valence vibrations appearing at 2960 (s-m), 2920 (m), and 2870 (s). Unfortunately, the high reactivity of the cumulene, which is also displayed by the parent hydrocarbon[28] prevented further study of this interesting cumulene. As far as the mode of formation of **12** is concerned it could be produced by base-catalyzed isomerization of the not isolated vinylbutatriene (**11**). For the origin of benzene many routes can be proposed; although its formation is not surprising,[23,26] with the scant experimental evidence a decision between these alternatives is presently hardly possible.

Experimental Section

General: UV: Cary-14. IR: Perkin–Elmer 221 and Beckman IR-8. MS (70 eV): Varian MAT CH-5. GC: Varian-Aerograph 1740–1. NMR: Varian A-60 in $CDCl_3$, if not given otherwise; TMS as internal standard. Since the compounds prepared in this study are all air-sensitive the experiments were carried out under nitrogen.

3-Acetoxy-1,4-pentadiyne (16): To a solution of 1,4-pentadiyn-3-ol[21] (19 g, 0.125 mol) in anhydrous pyridine (60 mL) was added slowly at 0 °C freshly distilled acetyl chloride (11.7 g, 0.15 mol). When the addition was complete the temperature was increased to room temp. and the brown reaction mixture was extracted with diethyl ether (2 × 200 mL). The pyridine was removed from the combined ethereal extracts by careful washing with water (5 × 150 mL) and 0.1 M hydrochloric acid. After neutralization with hydrogencarbonate solution and drying with sodium sulfate, the solvent was removed by rotary evaporation. The remaining yellow oil was vacuum-transferred under high vacuum at 40 °C: 10.8 g (71%) of **16** as colorless oil (b.p./16 Torr: 61 °C). ^{1}H NMR: δ = 2.14 (s, 3 H, acetate), 2.61 (d, J = 2.5 Hz, 2 H, –C≡C–H), 6.00 (t, J = 2.5 Hz, 1 H, –CH–) ppm. IR (film): $\tilde{\nu}$ = 3310 cm^{-1} (s) and 2150 (m, –C≡C–H), 1750 (s), 1230 (s), 1050 (s, acetate). MS (EI): m/z = 122 (3) [M^+], 107 (5), 80 (20), 79 (25), 63 (72), 62 (71), 43 (100). $C_7H_6O_2$ (122.12): calcd. C 68.84, H 4.95; found C 70.13, H 5.19 (the unstable ester turns yellow quickly during weighing, probably a reason for the faulty elemental analysis).

2,3-Hexadien-5-yne (8): To a suspension of lithium (1.8 g, 0.26 mol) in 80 mL of anhydrous ether was added a solution of 15.6 g (0.11 mol) of methyl iodide in 50 mL of ether at such a rate as to keep the reaction mixture gently refluxing. After completion of the addition the mixture was refluxed for 1 h and the prepared methyllithium solution transferred under nitrogen to a dropping funnel of a second three-necked reaction flask containing a suspension of copper(I) iodide (9.7 g, 0.05 mol) in 150 mL of anhydrous ether at –15 °C. When the methyllithium was added (keeping the reaction temperature at all times below –10 °C) the lemon yellow methyl copper precipitated but soon dissolved again to provide a grey cuprate solution. This solution was cooled to –15 °C and 5.3 g (0.04 mol) of **16** in 100 mL of ether was added slowly. When the addition was complete the temperature was raised to room temperature and the mixture stirred for 4 h. For work-up 150 mL of aqueous sat. ammonium chloride solution was added at –10 °C, the ether phase was separated and the aqueous phase extracted several times with ether. The combined organic phases were neutralized with hydrogencarbonate solution, washed with water, and dried with sodium sulfate. When the solvent was subsequently removed by distillation some 1,2-pentadien-4-yne (**17**) was lost as shown by GC-analysis (Carbowax, 55 °C). The remaining oily residue was separated from polymeric components by vacuum transfer (0.001 Torr) and subjected to preparative gas chromatography (Carbowax, 55 °C). Four main fractions were isolated.

Fraction 1. 1,2-Pentadien-4-yne (17): The volatile, polymerization-prone colorless liquid (0.3 g, 12%) had spectroscopic data identical with those reported in the literature.[21,22]

Fraction 2. 4-Methyl-1,2,4-hexatriene (18): 0.12 g, 3.5%; unstable colorless liquid that quickly turns brown, then black at room. temp.). ^{1}H NMR: δ = 1.65 (ps-s, 3 H, CH_3), 1.75 (ps-s, 3 H, CH_3), 4.92 (br. d, J = 7.0 Hz, 2 H, C=C=CH_2), 5.40 (m, 1 H, –CH=C), 5.80 (t, J = 7.0 Hz, 1 H, –CH=C=). IR (film): $\tilde{\nu}$ = 1940 cm^{-1} (s, C=C=C), 2970 (s), 2918 (s), 2860 (s), 1620 (w, C=C), 1435 (s), 1375 (s), 1105 (m), 875 (s), 840 (s, C=C=CH_2). To the NMR solution of this fraction a small excess of TCNE was added and the mixture

heated at 50 °C until all allene signals had vanished (ca. 6 h): **4,4,5,5-Tetracyano-1,6-dimethyl-3-methylidenecyclohexene (20):** ^{1}H NMR: δ = 1.62 (d, J = 7.0 Hz, 3 H, =CCH$_3$), 1.97 (s, 3 H, CH$_3$), 3.29 (m, 1 H, ring CH), 5.70 and 5.94 (2 × ps-s, 1 H each, =CH$_2$), 6.27 (br. ps-s, 1 H, endocyclic =CH) ppm. Since only very small amounts of this unstable material was available no further spectra were recorded.

Fraction 3. 2,3-Hexadien-5-yne (8): 1.14 g, 28%; colorless liquid. ^{1}H NMR: δ = 1.73 (dd, J_1 = 6.8, J_2 = 3.8 Hz, 3 H, CH$_3$), 2.84 (dd, J_1 = 1.6, J_2 = 2.2 Hz, 1 H, –C≡CH), 5.17–5.64 (br. m, –HC=C=CH–) ppm. IR (CCl$_4$): $\tilde{\nu}$ = 3321 cm^{-1} (s) and 2110 (w, –C≡CH), 1968 (s, –HC=C=CH–), 2959 (w), 2931 (w), 1442 (m), 1373 (m). MS (70 eV): m/z = 78 (100) [M$^+$], 63 (25), 52 (50), 51 (55), 50 (50), 39 (27). UV (ethanol): λ_{max} (log ε) = 216 nm (3.94). C$_6$H$_6$ (78.11): calcd. C 92.26, H 7.74; found C 91.84, H 7.94. For the base-catalyzed isomerization **8** (100 mg; 1.28 mmol) was treated in a NMR tube with 1 mL of a 0.113 N solution of potassium *tert*-butoxide in *tert*-butyl alcohol for 5 h at 60 °C under nitrogen. The reaction mixture was taken up in 10 mL of ether, the organic phase was dried with sodium sulfate and subjected to GC separation (Carbowax, 55 °C). As the sole isomerization product **2,4-hexadiyne** (**4**) was isolated in quantitative yield (95 mg, 95%) as shown by its spectroscopic and analytical data.[10]

Fraction 4. 3-Methyl-2,4,5-heptatriene (19): 0.11 g, 2.5%; colorless, unstable liquid. ^{1}H NMR: δ = 1.59 (m, 3 H, CH$_3$), 1.67 (s, 3 H, CH$_3$), 1.82 (m, 3 H, CH$_3$), 5.35 (m, 2 H, CH=CMe and C=C=CHMe), 5.77 (m, 1 H, =CMe–CH=C=) ppm. IR (CCl$_4$): $\tilde{\nu}$ = 3050 cm^{-1} (w), 3000 (w), 2980 (m-s), 2920 (s), 2857 (m), 1940 (m, C=C=C), 878 (s), 818 (s), 720 (s). UV (ethanol): λ_{max} (log ε) = 221 nm (4.50). MS (70 eV): m/z = 108 (65) [M$^+$], 93 (10), 91 (91), 80 (24), 78 (80), 65 (18), 53 (17), 39 (23). To the NMR solution of this fraction a small excess of TCNE was added and the mixture heated at 50 °C until all allene signals had vanished (ca. 6 h): **4,4,5,5-Tetracyano-3-ethylidene-1,6-dimethylcyclohexene (21):** Off-white needles (ethanol), m.p. 121–122 °C. ^{1}H NMR: δ = 1.62 (d, J = 7.0 Hz, 3 H, –CHCH$_3$–), 1.97 (m, 6 H, 2 × CH$_3$), 3.30 [m, 1 H, –C(Me)H–], 6.35 (m, 2 H, olefinic H) ppm. IR (KBr): $\tilde{\nu}$ = 2255 cm^{-1} (w, CN), 1620 (m, C=C), 820 (s), 807 (s). MS (70 eV): m/z = 236 (100) [M$^+$], 221 (58), 194 (71), 182 (44), 171 (37), 144 (32), 108 (84), 93 (92), 91 (35), 77 (40), 51 (35), 41 (39), 39 (58). UV (ethanol): λ_{max} (log ε) = 242 nm (3.21).

1-Acetoxy-2,4-pentadiyne (22): To a solution of 22.2 g (0.28 mol) of 2,4-pentadiyn-1-ol[24] in 500 mL of anhydrous pyridine 25.0 g (0.28 mol) of freshly distilled acetyl chloride was added at 0 °C at such a rate as to keep the temperature of the reaction mixture below 5 °C. After stirring for 2 h the reaction was worked-up as described above. Vacuum-transfer furnished 27 g (79%) of **22**, colorless oil (b.p./13 Torr: 74–75 °C). ^{1}H NMR: δ = 2.09 (s, 3 H, CH$_3$), 2.28 (t, J = 1.0 Hz, 1 H, –C≡CH), 4.73 (d, J = 1.0 Hz, 2 H, –CH$_2$–) ppm. IR (CDCl$_3$): $\tilde{\nu}$ = 3310 cm^{-1} (s) and 2060 (w, diyne unit), 1750 (s), 1215 (s) and 1027 (m, acetate). UV (ethanol): λ_{max} (log ε) = 209 nm (2.41), 218 (2.56), 228 (2.64), 241 (2.67), 254 (2.46). C$_7$H$_6$O$_2$ (122.1): calcd. C 68.84, H 4.95; found C 68.23, H 5.50.

3-Methyl-1,2-pentadien-4-yne (15): To a solution of lithium dimethyl cuprate prepared as described above from 4.0 g (0.57 mol) of lithium, 41.2 g (0.29 mol) of methyl iodide and 21.7 g (0.114 mol) of copper(I) iodide in 450 mL of diethyl ether 7.0 g (0.057 mol) of **22** in 100 mL of ether was added at –10 °C. After stirring at room temp. for 3 h the reaction mixture was hydrolyzed with satd. ammonium chloride solution. The insoluble material was removed by filtration, and the filtrate was extracted thoroughly with ether. The combined organic phases were treated successively with 0.1 M hydrochloric acid, satd. hydrogencarbonate solution and water before they were dried with sodium sulfate. The major part of the solvent was removed by distillation and the remaining higher-boiling fraction was purified by vacuum-transfer. Separation by preparative gas chromatography (Carbowax, 60 °C) yielded four fractions (ratio: 1.9:0.7:2.9:1, no quantitative separation was performed).

Fraction 1. 2,3-Dimethyl-1,3,4-pentatriene (23):[25] ^{1}H NMR: δ = 1.87 (m, 6 H, 2 × CH$_3$), 4.91 (m, 4 H, 2 × =CH$_2$) ppm. IR (CCl$_4$): $\tilde{\nu}$ = 3097 cm^{-1} (w), 1940 (s, C=C=C), 1620 (m, C=C), 850 (s, =CH$_2$). UV (ethanol): λ_{max} (log ε) = 214.5 nm (4.30). MS (70 eV): m/z = 94 (100) [M$^+$], 79 (60), 77 (70), 53 (45), 51 (55), 39 (76). A sample of **23** in benzene was treated at 50 °C with a slight excess of TCNE to provide **4,4,5,5-Tetracyano-1,2-dimethyl-3-methylidenecyclohexene (25):** ^{1}H NMR: δ = 1.97 (br. s, 6 H, 2 × CH$_3$), 3.17 (m, 2 H, –CH$_2$–), 5.85 (m) and 6.02 (m, 2 H, =CH$_2$) ppm.

Fraction 2. 1,2-Pentadien-4-yne (17): Identified by spectral comparison (see above).

Fraction 3. 3-Methyl-1,2-pentadien-4-yne (15): Colorless oil. ^{1}H NMR: δ = 1.83 (t, J = 3.2 Hz, 3 H, CH$_3$), 2.92 (ps-t, J = 1.4 Hz, 1 H, C≡CH), 4.91 (dq, J_1 = 3.2, J_2 = 1.4 Hz, 2 H, =C=CH$_2$) ppm. IR (CCl$_4$): $\tilde{\nu}$ = 3310 cm^{-1} (s) and 2095 (m, C≡CH), 1943 (s) and 855 (s, C=C=CH$_2$). UV (ethanol): λ_{max} (log ε) = 213 nm (4.17). MS (70 eV): m/z = 78 (100) [M$^+$], 77 (60), 63 (39), 52 (79), 51 (95), 50 (64), 39 (35). The hydrocarbon is volatile and unstable preventing an exact elemental analysis.

Fraction 4. Toluene (24): Identified by comparison with an authentic sample.

1,2,3,4-Hexatetraene (12): Within 20 min a solution of *n*-butyllithium (10.3 g, 0.075 mol) in 30 mL of anhydrous tetrahydrofuran was added at –10 °C to a suspension of propargyl triphenylphosphonium bromide (**28**)[29] (27.4 g, 0.072 mol) in 150 mL of tetrahydrofuran. The reaction mixture turned yellow during the addition, and when it was complete, the precipitate had dissolved and an intense yellow solution been formed. After additional stirring (30 min) at –10 °C the reaction temperature was lowered to –40 °C and acrolein (3.92 g, 0.07 mol) in 30 mL of tetrahydrofuran was added during 20 min. The now orange-red solution was stirred at 0 °C for 2 h during which time an amorphous precipitate formed. To the reaction mixture was added 200 mL of pentane followed by 150 mL of a saturated ammonium chloride solution. The organic phase was separated and thoroughly washed with ice water to remove the main part of the THF, a process accompanied by continuous production of polymeric material. The pentane was removed in vacuo (100–200 Torr, 10 °C) and the remaining turbid solution directly subjected to GC separation (Carbowax, 70 °C, ratio **12**:benzene ca. 0.55:1). The spectroscopic data of the isolated droplet of **12** are discussed in the main section.

[1] A. Krüger, H. Hopf, *Chem. Eur. J.* **2001**, *7*, 4378–4385.
[2] We thank Prof. Dr. L. Ernst (Technical University Braunschweig) for the calculation of these values by using the MOLGEN program (Chr. Benecke, R. Grund, R. Hohberger, A. Kerber, R. Laue, Th. Wieland, University of Bayreuth, Version 3, **1995**).
[3] H. Hopf, *Chem. Ber.* **1971**, *104*, 1499–1506.
[4] Ashe has described the formation of **8** as a side product in the CuCl-catalyzed reaction of ethynylmagnesium bromide with 3-bromobutyne; however, with the exception of the ^{1}H NMR spectroscopic data no other spectroscopic data of **8** were re-

ported: A. J. Ashe, III, W.-T. Chan, *Tetrahedron Lett.* **1975**, *16*, 2749–2752.

[5] T. C. Dinadayalane, U. D. Priyakumar, G. N. Sastry, *J. Phys. Chem. A* **2004**, *108*, 11433–11448.

[6] H. Maurer, Ph. D. Dissertation, Karlsruhe, **1977**.

[7] 1,5-Hexadiyne (bipropargyl, **1**): a) Synthesis: L. Brandsma, *Synthesis of Acetylenes, Allenes and Cumulenes – Methods and Techniques*, Elsevier, Amsterdam, **2004**, p. 56; b) Structure: D. L. Powell, P. Klaeboe, A. Phongsatha, B. N. Cyvin, S. J. Cyvin, H. Hopf, *J. Mol. Struct.* **1977**, *41*, 203–213; M. Traetteberg, P. Bakken, R. Seip, S. J. Cyvin, B. N. Cyvin, H. Hopf, *J. Mol. Struct.* **1979**, *51*, 77–85; G. O. Braathen, C. J. Nielsen, P. Klaeboe, H. Hopf, *J. Mol. Struct.* **1981**, *74*, 233–253; c) Preparative uses: F. Sondheimer, Y. Amiel, R. Wolosky, *J. Am. Chem. Soc.* **1957**, *79*, 6263–6267 and later publications in this series.

[8] 1,4-Hexadiyne (**2**): a) Synthesis: L. Brandsma, *Synthesis of Acetylenes, Allenes and Cumulenes – Methods and Techniques*, Elsevier, Amsterdam, **2004**, p. 114; b) Preparative uses: A. J. Ashe, W.-T. Chan, *J. Org. Chem.* **1979**, *44*, 1409–1413.

[9] 1,3-Hexadiyne (**3**): a) Synthesis: L. Brandsma, *Synthesis of Acetylenes, Allenes and Cumulenes – Methods and Techniques*, Elsevier, Amsterdam, **2004**, p. 95; b) Structure: S. Jouve, *C. R. Hebd. Seances Acad. Sci.* **1963**, *257*, 121.

[10] 2,4-Hexadiyne (**4**): a) Synthesis: L. Brandsma, *Synthesis of Acetylenes, Allenes and Cumulenes – Methods and Techniques*, Elsevier, Amsterdam, **2004**, p. 93; b) Structure: J. W. White, *J. Mol. Struct.* **1982**, *79*, 188–214; c) Preparative uses: R. West, W. Priester, *J. Am. Chem. Soc.* **1976**, *98*, 8426–8432; J. Klein, J. Y. Becker, *J. Chem. Soc. Perkin Trans. 2* **1973**, 599–603.

[11] 1,3-Hexadien-5-yne (**5**): a) Synthesis: L. Brandsma, *Synthesis of Acetylenes, Allenes and Cumulenes – Methods and Techniques*, Elsevier, Amsterdam, **2004**, p. 354; b) Structure: J. E. Baldwin, V. P. Reddy, *J. Am. Chem. Soc.* **1987**, *109*, 8051–8056; c) Preparative uses: H. Hopf in: *Modern Arene Chemistry* (Ed.: D. Astruc), Wiley-VCH, **2002**, chapter 5, p. 169; G. Zimmermann, *Eur. J. Org. Chem.* **2001**, 457–471.

[12] 1,5-Hexadien-3-yne (divinylacetylene, **6**): a) Synthesis: H. Hopf, L. Eisenhuth, V. Lehne, L. Ernst, *Chem. Ber.* **1986**, *119*, 1105–1109 and refs. cited therein; b) Structure: E. Toernung, C. J. Nielsen, P. Klaeboe, H. Hopf, V. Schüll, *J. Mol. Struct.* **1981**, *71*, 71–89; c) Preparative uses: A. L. Klebanski, M. Jelenjewski, V. Tschuganov, *Zh. Obshch. Khim. (J. Gen. Chem. U. S. S. R.)* **1947**, *17*, 1436–1450 (*Chem. Abstr.* **1948**, *42*, 2920).

[13] 1,2-Hexadien-5-yne (propargylallene, **7**): a) Synthesis: H. Hopf, *Chem. Ber.* **1971**, *104*, 3087–3095; H. Hopf, *Angew. Chem.* **1970**, *82*, 703; *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 732; b) Structure: P. Klaeboe, A. Phongsatha, B. N. Cyvin, S. J. Cyvin, H. Hopf, *J. Mol. Struct.* **1978**, *43*, 1–8; R. Seip, P. Bakken, M. Traetteberg, H. Hopf, *Acta Chem. Scand., Ser. A* **1981**, *35*, 365–371; P. Bischof, R. Gleiter, H. Hopf, F. T. Lenich, *J. Am. Chem. Soc.* **1975**, *97*, 5467–5472; c) Preparative uses: H. Hopf, *Tetrahedron Lett.* **1972**, *13*, 3571–3574; K. A. Black, S. Wilsey, K. N. Houk, *J. Am. Chem. Soc.* **1998**, *120*, 5622–5627.

[14] This paper.

[15] 1,2-Hexadien-4-yne (**9**): H. Hopf, *Chem. Ber.* **1971**, *104*, 3087–3095.

[16] 1,2,4,5-Hexatetraene (biallenyl, **10**): a) Synthesis: H. Hopf, *Angew. Chem.* **1970**, *82*, 703; *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 732; H. Hopf, J. Kleinschroth, I. Böhm, *Org. Synth.* **1981**, *60*, 41–48; b) Structure: D. H. Christensen, H. Hopf, P. Klaeboe, D. L. Powell, *Spectr. Chim. Acta* **1973**, *29A*, 7–16; M. Traetteberg, G. Paulen, H. Hopf, *Acta Chem. Scand.* **1973**, *27*, 2227–2229; B. Pedersen, J. Schaug, H. Hopf, *Acta Chem. Scand., Ser. A* **1974**, *28*, 846–850; c) Preparative uses: H. Hopf, *Angew. Chem.* **1972**, *84*, 471–472; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 419–420; H. Hopf, G. Schön, *Liebigs Ann. Chem.* **1981**, 165–180.

[17] 1,2,3,5-Hexatetraene (vinylbutatriene, **11**): H. Maurer, H. Hopf, *Angew. Chem.* **1976**, *88*, 687 –688; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 628–629.

[18] 3-Methylen-1-penten-4-yne (2-ethynyl-1,3-butadiene, **13**): a) Synthesis: H. Hopf, *Chem. Ber.* **1971**, *104*, 1499–1506; b) Structure: H. Priebe, C. J. Nielsen, P. Klaeboe, H. Hopf, H. Jäger, *J. Mol. Struct.* **1987**, *158*, 249–257; c) preparative uses: H. Hopf, H. Bader, H. Jäger, *Chem. Ber.* **1989**, *122*, 1193–1198.

[19] 3-Methyl-1,4-pentadiyne (**14**): a) Synthesis: A. J. Ashe, W.-T. Chang, *Tetrahedron Lett.* **1975**, *16*, 2749–2752; b) Structure: W. R. Roth, V. Staemmler, M. Neumann, C. Schmuck, *Liebigs Ann.* **1995**, 1061–1118.

[20] J. L. Luche, E. Barreiro, J. M. Dollat, P. Crabbé, *Tetrahedron Lett.* **1975**, *16*, 4615–4618; P. Rona, P. Crabbé, *J. Am. Chem. Soc.* **1969**, *91*, 3289–3292.

[21] E. R. H. Jones, H. H. Lee, M. C. Whiting, *J. Chem. Soc.* **1960**, 3483–3489.

[22] T. L. Chwang, R. West, *J. Am. Chem. Soc.* **1973**, *95*, 3324–3330; E. R. H. Jones, H. H. Lee, M. C. Whiting, *J. Chem. Soc.* **1960**, 341–346.

[23] H. Hopf, *Chem. Ber.* **1971**, *104*, 3087–3095.

[24] J. B. Armitage, E. R. H. Jones, M. C. Whiting, *J. Chem. Soc.* **1952**, 1993–1998.

[25] M. L. Roumestant, J. P. Dulcère, J. Goré, *Bull. Soc. Chim. France* **1974**, 1119–1123.

[26] H. Hopf, *Tetrahedron Lett.* **1970**, *11*, 1107–1109 and refs. cited therein.

[27] E. J. Corey, R. A. Ruden, *Tetrahedron Lett.* **1973**, *14*, 1495–1499.

[28] J. L. Ripoll, *J. Chem. Soc. Chem. Commun.* **1976**, 235–236; J. L. Ripoll, A. Thullier, *Tetrahedron* **1977**, *33*, 1333–1336.

[29] K. Eiter, H. Oediger, *Justus Liebigs Ann. Chem.* **1965**, *682*, 62–70.

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