

SYNTHESIS OF MONO- AND DI-ACETYLENIC HYDROCARBONS
CONTAINING QUATERNARY CARBON ATOMS

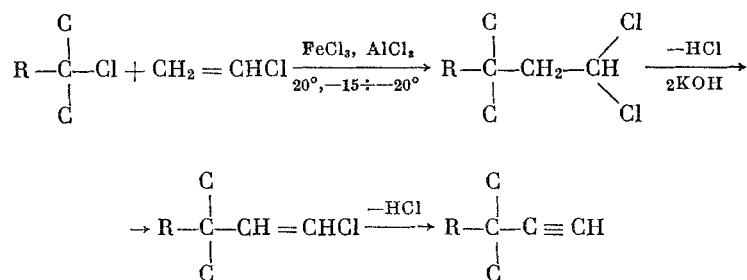
(UDC 547.362)

A. P. Meshcheryakov and L. V. Petrova

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR
Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 8,
pp. 1488-1497, August, 1964
Original article submitted December 24, 1962

Monosubstitued alkynes can be prepared from 1,2-dibromoalkanes [1], from monohaloalkenes with halogen at the double bond, and also from 1,1- and 2,2-dichloroalkanes formed by the reaction of aldehydes and ketones with phosphorus pentachloride.

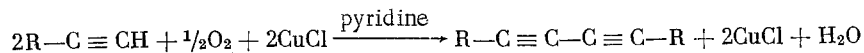
In contrast with the widely studied method of preparing monosubstituted acetylenes from 2,2-dichloroalkanes, in the present work we used C₆-C₁₀ 1,1-dichloroalkanes containing quaternary carbon atoms prepared in accordance with the scheme:



We prepared the lower dichloroalkanes—1,1-dichloro-3,3-dimethylbutane and 1,1-dichloro-3,3-dimethylpentane—by Schmerling's method [2] in presence of anhydrous ferric chloride in yields of 48-70%. However, the higher chloroalkanes, e.g. 2-chloro-2,3-dimethylbutane, 2-chloro-2,3,3-trimethylbutane, and 2-chloro-2,4,4-tetramethylpentane, mainly lose HCl under the given conditions with formation of alkenes and also their dimers. The same chloroalkanes react with vinyl chloride at between -15 and -20° only in presence of AlCl₃ with formation of the corresponding 1,1-dichloroalkanes in yields of 35-50% (Table 1). As will be seen from Table 1, the yields of 1,1-dichloroalkanes depend on the structure of the original tertiary chloroalkanes, the nature of the catalyst used, and the reaction temperature.

For the preparation of acetylenic hydrocarbons the 1,1-dichloroalkanes were heated over KOH in presence of small amounts of diethylene glycol. The elimination of HCl went in stages: monochloroalkenes were first formed, and then these gave acetylenic hydrocarbons. Thus, together with the monoacetylenic hydrocarbons, we isolated for the first time and characterized the following monochloroalkenes: 1-chloro-3,3,4-trimethyl-1-pentene, 1-chloro-3,3,4,4-tetramethyl-1-pentene, and 1-chloro-3,3,5,5-tetramethyl-1-hexene (Table 2). By the elimination of one molecule of HCl from the monochloroalkenes and two molecules of HCl from the 1,1-dichloroalkanes by heating them with solid KOH in presence of small amounts of diethylene glycol we prepared the known monoacetylenic hydrocarbons 3,3-dimethyl-1-butyne and 3,3-dimethyl-1-pentyne and the previously unknown 3,3,4-trimethyl-1-pentyne, 3,3,4,4-tetramethyl-1-pentyne, and 3,3,5,5-tetramethyl-1-hexyne (Table 3). By the method of oxidative dimerization [3] of monosubstituted acetylenes in presence of cuprous chloride and aluminum chloride we obtained the following diacetylenic hydrocarbons derived from butadiyne: the previously known 2,2,7,7-tetramethyl-3,5-octadiyne and the previously unknown 3,3,8,8-tetramethyl-4,6-decadiyne, 2,3,3,8,8,9-hexamethyl-4,6-decadiyne, 2,2,3,3,8,8,9,9-octamethyl-4,6-decadiyne, and 2,2,4,4,9,9,11,11-octamethyl-5,7-dodecadiyne (Table 4).

We must point out that the oxidative dimerization of highly branched alkynes containing nine or more carbon atoms under Zal'kind's conditions [3] goes with low yields, probably as a result of the low solubilities of these alkynes in the reaction medium. The yields of diacetylenic hydrocarbons are substantially increased by carrying out the oxidative dimerization by the action of oxygen in a pyridine medium with equimolecular amounts of the alkyne and cuprous chloride [4].



An examination of the properties of the diacetylenic hydrocarbons that we have synthesized shows (see Table 4) that the accumulation of methyl groups in the alkyl group increases the density of packing and raises the melting point of the hydrocarbon. Thus, in the case of 2,2,3,3,8,8,9,9-octamethyl-4,6-decadiyne, which has two adjacent quaternary carbon atoms in the alkyl group, the melting point has its highest value (287-288°). In 2,2,4,4,9,9,11,11-octamethyl-5,7-dodecadiyne (see Table 4) the quaternary carbon atoms in the alkyl groups are not linked directly, but through methylene groups, and there is the possibility, therefore, of freer rotation of the methyl groups of the diacetylenic hydrocarbon, and this is reflected in the very much lower melting point of the hydrocarbon, which is only 43.5°.

EXPERIMENTAL

Synthesis of 2,2,7,7-Tetramethyl-3,5-octadiyne

Preparation of 1,1-Dichloro-3,3-dimethylbutane. The alkylation was carried out in a rotating autoclave in presence of anhydrous ferric chloride at room temperature under a pressure of nitrogen (25 atm) for 4 h.

From 100 g of t-butyl chloride (cooled beforehand), 115 ml of vinyl chloride, and 10 g of FeCl₃ we obtained 112 g (67%) of 1,1-dichloro-3,3-dimethylbutane. For the properties of the dichloroalkane see Table 1.

Preparation of 3,3-Dimethyl-1-butyne. The dehydrochlorination was carried out in a rotating autoclave in presence of alcoholic KOH at 200-220° for 18 h. Before being discharged, the autoclave was cooled with ice. The reaction product was extracted with cold ethanol. 3,3-Dimethyl-1-butyne was distilled from the alcohol through a column of 24-plate efficiency. From 77 g of 1,1-dichloro-3,3-dimethylbutane, 135 g of KOH, and 15 ml of ethanol we obtained 3,3-dimethyl-1-butyne in 50% yield. For the properties of the hydrocarbon see Table 3.

The dehydrochlorination of 1,1-dichloro-3,3-dimethylbutane was carried out also over technical CaCO₃ at 280-300°, and 1-chloro-3,3-dimethyl-1-butene was obtained in 63% yield. Pieces of CaCO₃ (volume 150 ml) were placed in a quartz tube and heated to 280-300°. The dichloroalkane was introduced into the furnace from a dropping funnel at a space velocity of 0.2. The reaction product was condensed in a receiver cooled with ice and salt, and was then washed with water, dried over CaCl₂, and fractionated through a column of 24-plate efficiency. For fractionation we took 20 ml, and the fractions obtained were: I, b.p. 36-45°, 2.6 ml (mainly 3,3-dimethyl-1-butyne); II, b.p. 100-102°, 17.0 ml (the monochloroalkene C₆H₁₁Cl). For the properties of the monochloroalkene see Table 2. The dehydrochlorination of 1-chloro-3,3-dimethyl-1-butene was carried out over KOH in butyl alcohol [5] in a round-bottomed flask fitted with reflux condenser at 200-220° for 7-8 h. The hydrocarbon obtained was distilled from the reaction flask on a water bath.

From 65 g of 1-chloro-3,3-dimethyl-1-butene, 200 g of KOH, and 20 g of butyl alcohol we obtained 32.2 g (70%) of 3,3-dimethyl-1-butyne; b.p. 39-39.5°; d₄²⁰ 0.6742; n_D²⁰ 1.3730; Found: C 87.20; H 12.48%. C₆H₁₀. Calculated: C 87.79; H 12.21%. The literature [6] gives b.p. 39°. The hydrocarbon reacts with ammoniacal cuprous chloride and with silver nitrate and is therefore a monosubstituted acetylene.

Preparation of 2,2,7,7-Tetramethyl-3,5-octadiyne. The hydrocarbon was prepared by the method described by Zal'kind and Fundyler [3]. A mixture of 75 g of cuprous chloride, 118 g of ammonium chloride, 312 g of water, and 2 g of conc. HCl (sp. gr. 1.19) was prepared in a three-necked flask fitted with reflux condenser and mercury-sealed stirrer and was heated at 40° until dissolution was complete, after which 15 g of 3,3-dimethyl-1-butyne was added dropwise. Dimerization was carried out at 40°, and stirring was continued for 6 h. The reaction product was extracted with ether, the latter was driven off through the 24-plate column, and the residue of hydrocarbon was crystallized twice from methanol; m.p. 131-132°. For the properties of the hydrocarbon see Table 4.

Synthesis of 3,3,8,8-Tetramethyl-4,6-decadiyne

Preparation of 1,1-Dichloro-3,3-dimethylpentane. 2-Chloro-2-methylbutane was prepared by the hydrochlorination of 2-methyl-2-butene with gaseous HCl at 0°; b.p. 85-87°; d₄²⁰ 0.8591; n_D²⁰ 1.4065; Found MR 30.32;

TABLE 1

Dichloroalkane	Molecular formula	B. p., °C (p, mm)	d_4^{20}	n_D^{20}	Found MR	Calc. MR	Chlorine content, %		Yield, %
							Found	Calc.	
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{CH} \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	$\text{C}_6\text{H}_{12}\text{Cl}_2$	148—149	1,0324	1,4400	39,29	39,94	46,11	45,45	67,0
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{C}-\text{CH}_2-\text{CH} \\ \quad \quad \quad \\ \text{CH}_3 \quad \text{Cl} \quad \text{Cl} \end{array}$	$\text{C}_7\text{H}_{14}\text{Cl}_2$	50—52 (7)*	1,0297	1,4490	43,76	44,26	41,95	41,66	68,4
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{C}-\text{CH}_2-\text{CH} \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{Cl} \end{array}$	$\text{C}_8\text{H}_{16}\text{Cl}_2$	74—76 (13)	1,0246	1,4570	48,37	48,45	39,49	38,51	35,0
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{C}-\text{CH}_2-\text{CH} \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{Cl} \end{array}$	$\text{C}_8\text{H}_{16}\text{Cl}_2$	87—89 (8)	1,0614	1,4653	51,30	50,34	35,7	35,97	50,0
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3-\text{C}-\text{C}-\text{CH}_2-\text{CH} \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{Cl} \end{array}$	$\text{C}_{10}\text{H}_{20}\text{Cl}_2$	100—105 (15)	0,9924	1,4585	58,06	58,11	33,39	33,17	46,1

*The literature [2] gives: b.p. 50° (7 mm); d_4^{20} 1.0321; n_D^{20} 1.4500.

TABLE 3

Monoacetylene	Molecular formula	B. p., °C	d_4^{20}	n_D^{20}	Found MR	Calculated MR	Found %		Calculated, %		Yield, %
							C	H	C	H	
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{C}\equiv\text{CH} \\ \\ \text{CH}_3 \end{array}$	C_6H_{10}	38,5—39,0	0,6743	1,3735	27,77	27,84	87,16	12,50	87,79	12,21	50,0
3,3-Dimethyl-1-butyne											
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{C}\equiv\text{CH} \\ \\ \text{CH}_3 \end{array}$	C_7H_{12}	70—71*	0,7033	1,3956	32,72	32,47	87,17	12,99	87,50	12,50	23,0
3,3-Dimethyl-1-pentyne											
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{C}-\text{C}\equiv\text{CH} \\ \\ \text{CH}_3 \end{array}$	C_8H_{14}	97—98	0,7447	1,4124	36,79	37,08	87,10	12,82	87,27	12,73	70,0
3,3,4-Trimethyl-1-pentyne											
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{C}-\text{C}\equiv\text{CH} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	C_9H_{16}	118—119 M. p. 64°	—	—	—	—	86,64	12,93	87,03	12,97	33,0
3,3,4,4-Tetramethyl-1-pentyne											
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{C}-\text{C}\equiv\text{CH} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	$\text{C}_{10}\text{H}_{18}$	139—140	0,7691	1,4295	45,83	46,31	86,92	13,01	86,95	13,05	50,0
3,3,5,5-Tetramethyl-1-hexyne											

* The literature gives: b. p. 71° (760 mm); d_4^{20} 0,7290; n_D^{20} 1,4025.

calculated MR 30.16. 1,1-Dichloro-3,3-dimethylpentane was prepared in a three-necked flask at between -20 and -30° with constant stirring for 4 h. The reaction product was treated with water, neutralized with saturated potassium carbonate solution, washed with water, dried over CaCl_2 , and then vacuum-fractionated. From 106 g of 2-chloro-2-methylbutane, 64 g of vinyl chloride, and 4 g of AlCl_3 we obtained 115 g (68%) of 1,1-dichloro-3,3-dimethylpentane. For the properties of the dichloroalkane see Table 1.

Preparation of 3,3-Dimethyl-1-pentyne. 3,3-Dimethyl-1-pentyne was prepared by the dehydrochlorination of 1,1-dichloro-3,3-dimethylpentane in a rotating autoclave in presence of KOH in butyl alcohol at 130 - 140° for 10 h. The reaction product was poured from the autoclave, washed with water, dried over CaCl_2 , and fractionated through the 24-plate column. The yield of 3,3-dimethyl-1-pentyne was 14.1 g (23%). For the properties of the hydrocarbon see Table 3.

Preparation of 3,3,8,8-Tetramethyl-4,6-decadiyne. The hydrocarbon was prepared by oxidative dimerization [3] in 25% yield. For reaction we took 27.0 g of 3,3-dimethyl-1-pentyne, 135 g of CuCl , 174 g of NH_4Cl , 460 ml of H_2O , and 3 ml of conc. HCl (sp. gr. 1.19). For the properties of the hydrocarbon see Table 4.

Synthesis of 2,3,3,8,8,9-Hexamethyl-4,6-decadiyne

The hydrocarbon has been synthesized previously by the oxidative dimerization of 3,3,4-trimethyl-1-pentyne, which was prepared by the elimination of two molecules of HCl from 2,2-dichloro-3,3-dimethylpentane [7]. In this work we prepared 3,3,4-trimethyl-1-pentyne from 2-chloro-2,3,3-trimethylbutane and vinyl chloride in presence of AlCl_3 at between -13 and -15° in 35% yield. In the alkylation reaction we took 150 g of 2-chloro-2,3,3-trimethylbutane, 200 g of vinyl chloride, and 14 g of AlCl_3 . The reaction product was separated, washed with saturated potassium carbonate solution, dried over K_2CO_3 , and fractionated. For the properties of the dichloroalkane see Table 1.

The elimination of HCl from 1,1-dichloro-3,3,4-trimethylpentane was carried out with solid KOH in presence of a little diethylene glycol at 180 - 200° for 4 h. We took 80 g of the dichloroalkane, 162 g of KOH, and 10 ml of diethylene glycol. The yield of 3,3,4-trimethyl-1-pentyne was 70%. For the properties of the hydrocarbon see Table 3. We have described the procedure in the dimerization of 3,3,4-trimethyl-1-pentyne previously [8]. For reaction we took 34.3 g of 3,3,4-trimethyl-1-pentyne, 166 g of CuCl , 266 g of NH_4Cl , 708 g of water, and 3.8 g of conc. HCl (sp. gr. 1.19). The yield of 2,3,3,8,8,9-hexamethyl-4,6-decadiyne was 4.6 g (50.5%). For its properties see Table 4.

Synthesis of 3,3,4,4,8,8,9,9-Octamethyl-4,6-decadiyne

Preparation of 1,1-Dichloro-3,3,4,4-tetramethylpentane. The reaction of 2-chloro-2,3,3-trimethylbutane with vinyl chloride was carried out in a three-necked flask fitted with mercury-sealed stirrer in a dichloromethane medium with 100% excess of vinyl chloride in presence of 12% of AlCl_3 at between -15 and -20° for 6 h. The yield of the dichloroalkane was 50%. For its properties see Table 1.

Preparation of 3,3,4,4-Tetramethyl-1-pentyne. 3,3,4,4-Tetramethyl-1-pentyne was prepared by the elimination of two molecules of HCl from 1,1-dichloro-3,3,4,4-tetramethylpentane with KOH at 170 - 180° with stirring for 6 h. The yield of the hydrocarbon was 33%, and that of the monochloroalkene was 25-30%. For the properties of the hydrocarbon see Table 3.

Preparation of 3,3,4,4,8,8,9,9-Octamethyl-4,6-decadiyne. The hydrocarbon was prepared by the dimerization of 3,3,4,4-tetramethyl-1-pentyne. 1 ml of concentrated hydrochloric acid (sp. gr. 1.19) and 17 g of the monoacetylenic hydrocarbon dissolved in 50 ml of hexane were added to a solution of 81 g of CuCl and 110 g of NH_4Cl in 300 ml of water. The reaction mixture was heated in a water bath at 70 - 74° for 10 h. The reaction product was extracted with ether (200 ml). The ether was decanted, and extractions with three 100-ml portions of ether followed. The ethereal solution was washed with water and dried over CaCl_2 . Ether was driven off through the 24-plate column. By fractionation we isolated 10.5 g of unchanged 3,3,4,4-tetramethyl-1-pentyne, and the residue was a high-melting hydrocarbon, m.p. 287 - 288° (from a 3:1 mixture of hexane and ethanol); yield 2%. 3,3,4,4,8,8,9,9-octamethyl-4,6-decadiyne was also prepared by the oxidative dimerization of 3,3,4,4-tetramethyl-1-pentyne by Klebanskii's method [4].

A mixture of 60 ml of pyridine, 10.5 g of 3,3,4,4-tetramethyl-1-pentyne (dissolved in some of the pyridine), and 8.8 g of CuCl was prepared in a 250-ml long-necked flask. The reaction was carried out in presence of oxygen with agitation in a shaker. The end of the reaction was determined from the amount of oxygen absorbed (3.5 h was required). The yield of 3,3,4,4,8,8,9,9-octamethyl-4,6-decadiyne was 80%. For the properties of the hydrocarbon see Table 4.

Synthesis of 2,2,4,4,9,9,11,11,-Octamethyl-5,7-dodecadiyne

Preparation of 1,1-Dichloro-3,3,5,5-tetramethylhexane. 2-Chloro-2,4,4-trimethylpentane was prepared from Butlerov's "diisobutylene" by saturating it with HCl at 0° in presence of 5% of FeCl₃. The alkylation reaction was carried out under conditions analogous to those described above. For reaction we took 138 g of 2-chloro-2,4,4-trimethylpentane, 120 ml of vinyl chloride, and 8 g of AlCl₃. We obtained 91 g (45.1%) of 1,1-dichloro-3,3,5,5-tetramethylhexane. For the properties of the dichloroalkane see Table 1. In addition to the dichloroalkane we obtained the monochloroalkene (1-chloro-3,3,5,5-tetramethyl-1-hexene) in 13.4% yield. For its properties see Table 2.

Preparation of 3,3,5,5-Tetramethyl-1-hexyne. The hydrocarbon was prepared by the dehydrochlorination of 1,1-dichloro-3,3,5,5-tetramethylhexane with solid KOH in presence of diethylene glycol. The reaction was carried out in a three-necked flask with spherical condenser and mercury-sealed stirrer at 190-200° for 3 h. The hydrocarbon obtained was distilled from the reaction flask at 96°. It was dried over CaCl₂ and fractionated through the 24-plate column; yield 50%. For the properties of the hydrocarbon see Table 3.

Preparation of 2,2,4,4,8,8,11,11-Octamethyl-5,7-dodecadiyne. 10.4 g of 3,3,5,5-tetramethyl-1-hexyne was added dropwise to a solution of 37.2 g of cuprous chloride, 48.2 g of ammonium chloride, and 1.0 ml of conc. HCl (sp. gr. 1.19) in 127.5 ml of water warmed to 40° with the continuous passage of air. Heating was continued for 10 h. The hydrocarbon was extracted with ether, ether was driven off through the 24-plate column, and the solid hydrocarbon was crystallized from methanol; m.p. 43.5°; yield 2%. 2,2,4,4,8,8,11,11-Octamethyl-5,7-dodecadiyne was prepared also by oxidative dimerization by Klebanskii's method [4]. A mixture of 11 g of 3,3,5,5-tetramethyl-1-hexyne, 8 g of CuCl, and 80 ml of pyridine was prepared in a 250-ml long-necked flask. The reaction was carried out in presence of oxygen with agitation in a shaker for 4 h; yield 55%. For the properties of the product see Table 4.

SUMMARY

1. By the alkylation of t-alkyl chlorides with vinyl chloride in presence of metal halides the following dichloroalkanes were synthesized for the first time: 1,1-dichloro-3,3,4-trimethylpentane, 1,1-dichloro-3,3,4,4-trimethylpentane, 1,1-dichloro-3,3,5,5-tetramethylhexane.

2. By the dehydrochlorination of 1,1-dichloroalkanes over KOH in diethylene glycol monoacetylenic hydrocarbons containing quaternary carbon atoms were prepared for the first time.

3. The following diacetylenic hydrocarbons were prepared for the first time by oxidative dimerization: 3,3,8,8-tetramethyl-4,6-decadiyne, 2,3,3,8,8,9-hexamethyl-4,6-decadiyne, 2,2,3,3,8,8,9,9-octamethyl-4,6-decadiyne, and 2,2,4,4,9,9,11,11-octamethyl-5,7-dodecadiyne.

LITERATURE CITED

1. T. L. Jacobs, Collection 5 of "Syntheses of Acetylenes" [Russian translation], **II**, M. (1951).
2. L. Schmerling, *J. Amer. Chem.*, **68**, 1650 (1946).
3. Yu. S. Zal'kind and B. M. Fundyler, *Zh. obshch. khimii*, **26**, 530 (1936).
4. A. L. Klebanskii, L. V. Grachev, and O. M. Kuznetsova, *Zh. obshch. khimii*, **27**, 11, 2977 (1957).
5. A. I. Zakharova and R. A. Sapozhnikova, *Zh. obshch. khimii*, **22**, 1804 (1952).
6. A. E. Favorskii, Selected Works [in Russian], *Izd. AN SSSR*, M. (1940), p. 31.
7. A. P. Meshcheryakov and L. V. Petrova, *Izv. AN SSSR. Otd. khim. n.*, **1961**, 2251.

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.
