in 2 hours with the consumption of 1.2 moles of hydrogen. The reaction mixture gave an intense spot of methyl phosphate (R_{f_1} 0.15) and a faint spot of inorganic phosphate. The catalyst was filtered and washed with methanol; the washings and filtrate were combined. Water (20 ml.) was added, the mixture was extracted with ether and the extract dried. On removal of the solvent, 100 mg. of white needles was obtained which were recrystallized from aqueous ethanol; m.p. 64–65.5°. A mixture of this product and an authentic sample of phenylbenzylcarbinol[6] showed no depression of the melting point.

The aqueous layer, obtained above after extraction with ether, was adjusted to *p*H 8.0 with a barium hydroxide solution. Barium phosphate was removed by centrifugation and the supernate was decationized with Amberlite IR-120-H$^+$. The resulting acidic solution was again adjusted to *p*H 8.0 with a saturated barium hydroxide solution. After removal of excess barium ion with carbon dioxide, the solution was concentrated to 10 ml. and poured into acetone. The resulting precipitate was dried over P_2O_5 at 130°. *Anal.* Calcd. for CH_3O_4PBa: C, 4.85; H, 1.21; P, 12.53. Found: C, 5.12; H, 1.29; P, 12.50.

Alcoholysis of II with Hydrogen Chloride–Dioxane as the Catalyst.—To tubes containing a solution of II (2 mg.) in 0.2 ml. of the alcohol was added 0.2 ml. of hydrogen chloride–saturated dioxane. One series was incubated at 37° for 24 hours and the other for 72 hours. The reaction mixtures were chromatographed as described for the trifluoroacetic acid-catalyzed alcoholysis reactions.

Preparation of 1,2-Propanediol-1-phosphate (VI) by Phosphorylation of Propanediol with II.—To 2.0 g. of II was added 15 ml. of dry 1,2-propanediol. The mixture was saturated with dry hydrogen chloride gas. After 24 hours incubation at 37°, the salt disappeared with the simultaneous separation of sodium chloride. The excess hydrochloric acid was removed by aeration and the inorganic salt was centrifuged.

Water (60 ml.) and an excess of silver carbonate were added to the supernate, and the mixture was kept at room temperature overnight. After removal of the insoluble silver salt by centrifugation, the supernate was extracted exhaustively with ether, and the aqueous layer which contained silver ion was treated with hydrogen sulfide. From the silver ion-free solution the excess of hydrogen sulfide was removed by aeration and the solution was lyophilized. The residue which contained a small amount of propanediol was again dissolved in 100 ml. of water. This solution was adjusted to *p*H 8.0 with barium hydroxide solution, kept overnight at room temperature, treated with carbon dioxide and filtered. The filtrate was lyophilized to give a white powdery barium salt contaminated with propanediol, the latter was removed by washing the salt twice with acetone. The salt, dissolved in 20 ml. of water, was kept overnight in a refrigerator, and a small amount of material which separated was filtered. The filtrate was added to 40 ml. of acetone, and the resulting precipitate was centrifuged and dried over P_2O_5, yield 0.8 g.

An aqueous solution of 0.2 g. of this powder was treated with Amberlite IR-120-H$^+$. An equivalent amount of cyclohexylamine was added to the acidic solution. On lyophilization, 0.32 g. of residue was obtained which was dissolved in a small quantity of water and filtered. On addition of acetone, the filtrate gave white needles which were dried over P_2O_5 at room temperature; m.p. 168–169° dec. *Anal.* Calcd. for $C_{15}H_{35}O_5N_2P\cdot{}^1/_2H_2O$: C, 49.59; H, 9.92. Found: C, 49.26; H, 10.30.

HONGO, TOKYO, JAPAN

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[6] H. Limpricht and H. Schwanert, *Ann.*, **155**, 63 (1870).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BOSTON UNIVERSITY AND THE DANIEL SIEFF RESEARCH INSTITUTE WEIZMANN INSTITUTE OF SCIENCE]

Acetylene–Allene Isomerization of Nonadiyne-1,4[1]

BY WALTER J. GENSLER AND JOSEPH CASELLA, JR.

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Alkali at room temperature isomerizes nonadiyne-1,4 to nonadien-1,2-yne-4, and then to nonadiyne-2,4. The preparation and properties of the three hydrocarbons are described.

Nonadiyne-1,4 (I) with alkaline mercuric iodide furnishes a crystalline mercuric acetylide derivative in high yield.[2] The observation that exposure of nonadiyne-1,4 to alkali before forming the mercury compound decreases the yield indicated that alkali acts to change the hydrocarbon in some way. The present paper reports the results of a study of this action.

Isomerization of Nonadiyne-1,4.—It was found that nonadiyne-1,4 (I) in contact with alkali

$$\underset{\text{I}}{C_4H_9C{\equiv}CCH_2C{\equiv}CH} \longrightarrow$$

$$\underset{\text{II}}{C_4H_9C{\equiv}CCH{=}C{=}CH_2} \longrightarrow \underset{\text{III}}{C_4H_9C{\equiv}CC{\equiv}CCH_3}$$

isomerizes readily and cleanly to the allenic compound, nonadien-1,2-yne-4 (II); and that allene II under the same conditions isomerizes further to the conjugated diacetylene, nonadiyne-2,4 (III). Under the proper conditions, the latter two compounds could be isolated from the reaction mixture in acceptable yields. The isomerization could be followed conveniently by observing the change in intensity of the 220.5 mμ absorption of allene II, or by noting the intensities of the absorptions at 3.03 μ, which is the acetylenic hydrogen stretching vibration for nonadiyne-1,4; at 5.15 μ, the allenic stretching vibration for compound II; and at 4.91 μ, an unassigned vibration characteristic of the conjugated diyne III.

The changes in compound I are analogous to those observed in other terminal acetylenes,[3,4] and follow the generalization that in the compounds $RCH_2C{\equiv}CH$, $RCH{=}C{=}CH_2$ and $RC{\equiv}CCH_3$ the thermodynamic stability is least in the terminal acetylene and greatest in the methylacetylene. In addition to the factors pointed out before in interpreting this order of stability[5,6] the presence of conjugation in compounds II and III and the absence of conjugation in I should favor compounds II and III over I.

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[1] This is Paper VI in a series on skipped unsaturation.

[2] W. J. Gensler, A. P. Mahadevan and J. Casella, Jr., THIS JOURNAL, **78**, 163 (1956).

[3] T. L. Jacobs, R. Akawie and R. G. Cooper, *ibid.*, **73**, 1273 (1951).

[4] T. L. Jacobs in R. Adams, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 13.

[5] R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Academic Press, Inc., New York, N. Y., 1955, p. 134.

[6] E. R. H. Jones, G. H. Whitham and M. C. Whiting, *J. Chem. Soc.*, 3201 (1954).

The reaction conditions used in the isomerization of nonadiyne-1,4 are not harsh. For example, in one experiment, nonadiyne-1,4 (0.618 *M*) in aqueous alcohol solution containing alkali (0.47 *N*) was converted to nonadiyne-2,4 in less than a day at room temperature. In another run, 0.0084 *M* nonadiyne-1,4 in the presence of 0.012 *N* alkali was converted to the conjugated diyne III in less than a week at 25°. In the latter experiment the concentration of allene II reached a maximum at the end of 1.25 hours, so that it was evident that the conversion of skipped diyne I to allenic compound II was much faster than the conversion of allene II to conjugated diyne III. With certain substrates milder reaction conditions than those used here have effected acetylene–allene rearrangements. For example, butynoic ester isomerizes even with bicarbonate at 50°.[7] However, the conditions employed in the present work appear unusually mild for this kind of rearrangement in a purely hydrocarbon material.[8]

No indication of reversal in the reactions leading to II or to III was detected. Alkali with allene II led only to the conjugated diyne III and not to the skipped diyne I. Again, the conjugated diyne III, on standing under alkaline isomerization conditions, showed no tendency to form either allene II or skipped diyne I. These observations may be interpreted as indicating two consecutive irreversible reactions, in which the first, as mentioned above, is much faster than the second. Or, alternatively, they may signify an equilibrium set up rapidly between compounds I and II and lying far over to the side of II, which equilibrium is drained relatively slowly but eventually almost entirely in favor of the conjugated diyne III. It is hoped that further work using a more sensitive analytical procedure will establish the equilibrium[3,7] or non-equilibrium nature of the reactions.

Purification of Nonadiyne-1,4 (I).—In order to establish some basis for an analytical method it was necessary to obtain the three compounds as pure as possible. The starting material, nonadiyne-1,4, as obtained from the coupling of propargyl bromide and hexynylmagnesium bromide[2] contains an appreciable amount of allenic impurity, probably compound II. Displacement chromatography over silica gel[9] as well as regeneration of the nonadiyne-1,4 from its copper derivative did serve to remove this impurity. However, the method of choice, which originated in the observation that the total allene content in the distillate from a prolonged fractional distillation was less than in the original pot charge, consisted simply of destroying the allenic impurity in nonadiyne-1,4 by boiling the mixture at atmospheric pressure.[10] The heat treatment did not affect the nonadiyne-1,4, since the product obtained gave the same crystalline mercury derivative as before,[2] and since the infrared absorption spectrum (Fig. 1) is the same as that of the starting material, with the exception of the allenic absorptions (5.15 and 11.71 μ) which are absent. The very small absorption maximum at 4.9 μ was of some concern since the conjugated diyne III showed absorption at this point. However, for the following reasons it was unlikely that the conjugated diyne was present in significant amounts. First, nonadiyne-1,4 regenerated from its copper derivative—and accordingly free of all non-terminal acetylene—showed the same small maximum. Second, the ultraviolet absorption curve calculated for nonadiyne-1,4 containing as little as 2% of conjugated diyne III shows maxima characteristic of the latter, whereas the curve observed for nonadiyne-1,4 (Fig. 2) is free of these maxima and has only a maximum of low intensity at 263 mμ. A noteworthy property of nonadiyne-1,4 is its marked reluctance to show active hydrogen either with lithium aluminum hydride or with methylmagnesium iodide. Compound I must be an unusually weak acid even relative to other monosubstituted acetylenes.[11]

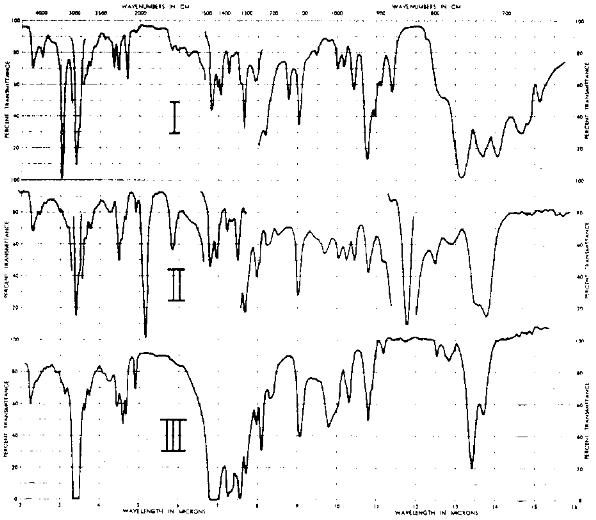

Fig. 1.—Infrared absorption spectra: I, nonadiyne-1,4; II, nonadien-1,2-yne-4; III, nonadiyne-2,4. Layers of neat liquid were used except where the absorption was too great; solutions in carbon tetrachloride were substituted at these points.

Preparation of Nonadiyne-2,4 (III).—The conjugated diacetylene III was prepared by alkylating diacetylene first with butyl bromide[12] to give octadiyne-1,3 and then with methyl iodide. The same material was obtained by isomerizing nonadiyne-1,4 with alkali. Actually the ease of the isomerization suggests that this kind of process could prove of gen-

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[7] G. Eglinton, E. R. H. Jones, G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.*, 3197 (1954).

[8] A variety of alkaline conditions have been used for prototropic acetylene-allene rearrangements more or less closely related to the rearrangement of nondiyne-1,4. *Cf.* E. R. H. Jones, G. H. Whitham and M. C. Whiting, *ibid.*, 3201 (1954); E. R. H. Jones, G. H. Mansfield and M. C. Whiting, *ibid.*, 3208 (1954); E. R. H. Jones, B. L. Shaw and M. C. Whiting, *ibid.*, 3212 (1954); G. H. Mansfield and M. C. Whiting, *ibid.*, 4761 (1956); J. D. Bu'Lock, E. R. H. Jones, P. R. Leeming and J. M. Thompson, *ibid.*, 3767 (1956); W. D. Celmer and I. A. Solomons, THIS JOURNAL, **75**, 1372, 3430 (1953); **74**, 3838 (1952); H. H. Schlubach and V. Wolf, *Ann.*, **568**, 141 (1950). Also note footnote 3.

[9] B. J. Mair, *J. Res. Natl. Bureau Standards*, **34**, 435 (1945).

[10] W. D. Celmer and I. A. Solomons, THIS JOURNAL, **75**, 3430 (1953), encountered a related instance of the disappearance of an allenic material during distillation.

[11] *Cf.* R. E. Dessy, J. H. Wotiz and C. H. Hollingsworth, *ibid.*, **79**, 358 (1957); J. H. Wotiz, C. A. Hollingsworth and R. E. Dessy, *J. Org. Chem.*, **20**, 1545 (1955).

[12] J. B. Armitage, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 1993 (1952).

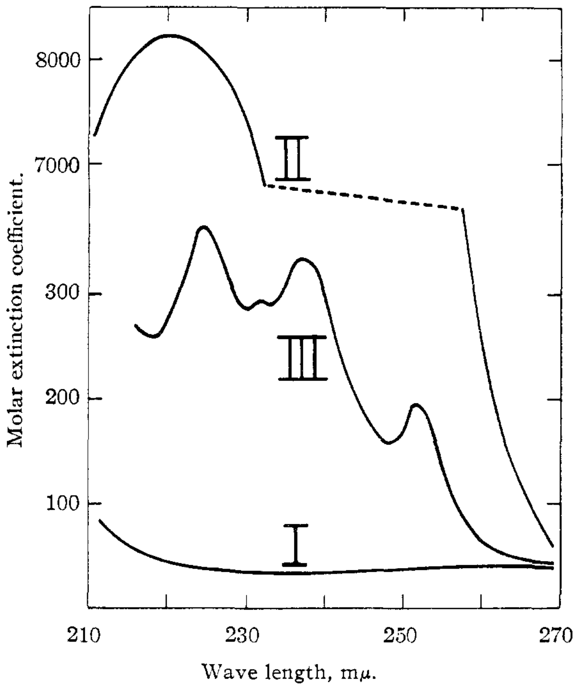

Fig. 2.—Ultraviolet absorption spectra: I, nonadiyne-1,4; II, nonadien-1,2-yne-4; III, nonadiyne-2,4.

eral use in the preparation of methyldiacetylenes. The ultraviolet absorption spectrum (Fig. 2) showed the maxima expected for a conjugated diyne.[13] The infrared absorption curve for compound III (Fig. 1) in showing no absorption due to terminal acetylene (3.03 μ) or to terminal allene (5.15 and 11.71 μ), provides evidence for the absence of compounds I and II. The peak at 4.91 μ, although unassigned, proved useful in estimating the concentration of nonadiyne-2,4 (III) mixed with compounds I and II.

Preparation of Nonadien-1,2-yne-4 (II).—Alkali isomerization of nonadiyne-1,4, when interrupted at the proper stage, provided a mixture of unchanged starting material and of nonadien-1,2-yne-4 (II). Removal of the residual starting material by precipitation as the copper derivative gave the allenic material II used in this work. Absence of all terminal acetylenic compounds was indicated by the absence of an absorption peak at 3 μ (Fig. 1). The peak at 4.9 μ, although of low intensity, is probably significant in indicating that the nonadien-1,2-yne-4 is contaminated with some nonadiyne-2,4 (III). The ultraviolet absorption (Fig. 2) has a prominent maximum at 220.5 mμ, which is much more intense than any of the maxima of compounds I or III. This maximum for nonadien-1,2-yne-4 falls in the region of the absorption maxima (219.5 to 230 mμ) for eneynes[14] and shows again that only one of the two double bonds of an allene is electronically conjugated to an adjacent unsaturation.[15] The fact that there is strong allenic absorption at 5.15 and at 11.71 μ (the overtone at 5.86 μ is also evident)[16] fixes the three-carbon allenic system at the end of the chain. This, together with the fact that the ultraviolet absorption shows conjugation in the molecule, is sufficient to determine the structure as in II. The presence of unsaturation between positions 4 and 5 was further shown by formation of valeric acid on ozonolysis. Nonadien-1,2-yne-4 (II) not only is unstable toward air, which property it has in common with the skipped and the conjugated diynes, but it also is thermally unstable at temperatures above 120°.

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Experimental[17]

Nonadiyne-1,4 Purification by Heat Treatment.—By making use of the infrared 3.03 and 5.15 μ absorptions, the nonadiyne-1,4[2] from hexynylmagnesium bromide and propargyl bromide[18] was estimated to consist of more than 90% of nonadiyne-1,4 and less than 10% of nonadien-1,2-yne-4. The concentration of nonadien-1,2-yne-4 in the nonadiyne-1,4, as determined by means of the 220.5 mμ absorption of the former compound, was approximately 6–8%. The preferred method of purifying nonadiyne-1,4 is given.

Nonadiyne-1,4 (12.5 g.) was held in an oil-bath at 180–190° under a reflux condenser for 4.5 hours. Pure nitrogen or helium was used to keep air away from the boiling liquid Distillation through a Claisen still-head gave water-white nonadiyne-1,4 (10.4 g. or 83% recovery), b.p. 77–77.5° (32 mm.), $n^{25}\text{D}$ 1.44990, density (25°) 0.8110.

Anal. Calcd. for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 90.10; H, 9.85.

That no rearrangement occurred during the heat treatment was shown by preparation of a mercury derivative the same as that obtained before.[2] After treatment with decolorizing carbon and crystallization from ethyl acetate, the pure white crystals melted at 113–114°; active hydrogen, calcd. for one active hydrogen in nonadiyne-1,4, 0.833%; found, using a saturated solution of lithium aluminum hydride in dibutyl ether held at room temperature for five minutes and then at 100° for five minutes, 0.0%; found, using 1 *M* methylmagnesium iodide in toluene at room temperature for five minutes, 0.0%. When the Grignard mixture was warmed at 100° for ten minutes, methane corresponding to 0.571% of active hydrogen was evolved; molecular refraction, calcd.[19] for nonadiyne-1,4 39.95, found 39.82. By a micro-method, the boiling point at atmospheric pressure was 163°. Ordinary distillation showed b.p. 165–166°.

A low intensity ultraviolet maximum was observed at 262 mμ (ε 41) with a 6.34×10^{-3} *M* solution in 95% alcohol (Fig. 2). In another determination using a recording

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(13) *Cf.* J. B. Armitage, *et al.*, *J. Chem. Soc.*, 1998 (1952).

(14) E. R. H. Jones and J. T. McCombie, *ibid.*, 261 (1943); I. M. Heilbron, E. R. H. Jones and co-workers, *ibid.*, **77**, 81, 84, 90 (1945); J. D. Chanley and H. Sobotka, THIS JOURNAL, **71**, 4140 (1949); G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, 3650 (1950); J. C. Hamlet, H. B. Henbest and E. R. H. Jones, *ibid.*, 2652 (1951); J. B. Armitage and M. C. Whiting, *ibid.*, 2005 (1952); I. Bell, E. R. H. Jones and M. C. Whiting, *ibid.*, 2597 (1957).

(15) *Cf.* W. D. Celmer and I. A. Solomons, *ibid.*, **75**, 1372 (1953).

(16) J. H. Wotiz and D. E. Mancuso, *J. Org. Chem.*, **22**, 207 (1957).

(17) Temperatures are uncorrected. Analyses were performed by Dr. Stephen M. Nagy (Microchemical Laboratory, Massachusetts Institute of Technology), by Dr. Carol K. Fitz (115 Lexington Avenue, Needham Heights 94, Mass.) and by Dr. E. Meier (Microchemical Laboratory, Weizmann Institute of Science, Rehovoth, Israel). Ultraviolet absorptions were determined with a Unicam spectrophotometer.

(18) This material was very kindly provided by Antara Chemicals Division of General Aniline and Film Corporation.

(19) A. I. Vogel, *et al.*, *J. Chem. Soc.*, 514 (1952).

spectrophotometer (Cary), an 8.17 × 10^{-3} *M* alcoholic solution showed λ_{max} 263 mμ (ε 26). There was no sign of the maximum noted before[2] at 214 mμ. In the infrared (Fig. 1), absorptions were evident at 3.03 μ (3300 cm.$^{-1}$), corresponding to acetylenic hydrogen, and at 4.42 μ (2260 cm.$^{-1}$), 4.56 μ (2190 cm.$^{-1}$) and 4.65 μ (2150 cm.$^{-1}$), corresponding to the carbon–carbon triple bonds. No allenic peaks appeared at 5.15 μ (1942 cm.$^{-1}$) or at 11.71 μ (853 cm.$^{-1}$).

Nonadiyne-1,4 Purification by Displacement Chromatography.—A jacketed column 170 cm. high, containing 140 g. of Davison activated silica gel (28–200 mesh), was prepared substantially according to Mair.[9] The column was cooled with circulating ice-water. After sweeping the column with pure nitrogen, the following materials were placed on the column in the order: 4 ml. of pentane, 17.8 g. of nonadiyne-1,4 containing allene, and 95% alcohol. A head of 1–9 mm. of pure nitrogen pressure forced liquid through the column at a suitable rate. Fractions of approximately 0.6 g. were taken; the over-all recovery was satisfactory. Fractions 4-16 (7.56 g.) showed decreasing intensities of absorption at 5.15 μ. Fraction 17 showed little if any absorption at 5.15 μ. Combined fractions 19–33 (8.9 g.) were distilled at b.p. 70–73° (24 mm.) to give 7.5 g. of nonadiyne-1,4 showing an infrared absorption curve essentially the same as in Fig. 1.

Nonadiyne-1,4 Purification by Regeneration from Its Copper Derivatives.—Freshly distilled nonadiyne-1,4 (7.51 g.) was added to a well-stirred mixture of cuprous chloride (10 g.), concentrated aqueous ammonia (400 ml.) and alcohol (400 ml.). A precipitate appeared immediately. The mixture was shaken vigorously and allowed to stand for 30 minutes. Filtration afforded a light-yellow solid, which was washed with water, alcohol and ether, and finally dried over calcium chloride in a vacuum desiccator. The dried product was extracted several times with 50-ml. portions of boiling ether until the ether no longer acquired a yellow color. The copper derivative, dried in a vacuum desiccator, weighed 9.0 g. (79%) and decomposed at 97–107°.

A mixture of powdered copper derivative (9.0 g.), 50 ml. of concentrated hydrochloric acid, 100 ml. of water and 100 ml. of benzene was refluxed for 2.5 hours. The benzene layer was separated from the filtered mixture and was dried over magnesium sulfate. The liquid remaining after removal of the benzene by distillation on the steam-bath through a 35-cm. column was distilled in a small Claisen flask. The main fraction (4.25 g., 75%), which boiled at 56–57° (15 mm.) and showed $n^{25}\text{D}$ 1.4506, was redistilled through a 4-inch Vigreux column to give pure nonadiyne-1,4, b.p. 53–54° (14 mm.) and $n^{25}\text{D}$ 1.4497. The infrared absorption curve for this material was the same as that of the original nonadiyne-1,4 excepting the allenic absorptions at 5.15 and 11.71 μ, which were absent.

Anal. Calcd. for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.7; H, 10.3.

Regeneration of nonadiyne-1,4 was also possible (a) by stirring a slightly acidified mixture of copper derivative, saturated aqueous ammonium chloride solution and ether at room temperature for one day, and (b) by a metathetical process in which acetylene gas plus the copper derivative furnished insoluble Cu_2C_2 and free nonadiyne-1,4.

Preparation of Nonadien-1,2-yne-4.—Nonadiyne-1,4 (4.1 g., 0.034 mole) in 50 ml. of 95% alcohol was treated under nitrogen with 5.0 ml. of 10% aqueous sodium hydroxide and allowed to stand at room temperature (*ca.* 18°) for 3 hours. The mixture, cooled in ice, was acidified with an ice-cold solution of 2 ml. of concentrated hydrochloric acid in 40 ml. of water. The organic material was removed by extraction with four 40-ml. portions of pentane, the pentane extracts were washed with water to remove acid, and the nearly colorless solution dried over calcium chloride. Solvent was removed from the dry solution by distillation (inside temperature not over 100°), and the residue was distilled in a Claisen flask. Water-white distillate (3.55 g.), b.p. 84° (22 mm.), which showed a marked diminution in the terminal acetylenic absorption peak at 3.03 μ and an intense absorption at 5.15 μ, was collected.

Residual nonadiyne-1,4 was removed by precipitation of its copper salt as follows. Concentrated aqueous ammonia (40 ml.) with 4.0 g. of cuprous chloride was magnetically stirred for several hours in a stoppered flask; 40 ml. of 95% alcohol was added, the stirred mixture was cooled in an ice-bath, and the above distillate added with the help of 15 ml. of 95% alcohol. After stirring for 5 minutes in the ice-bath, 50 ml. of pentane and 15 ml. of water were added, the mixture was stirred further for several minutes, and then extracted with pentane. Filtration through a filter-aid (Hyflo-Supercel) removed solids and permitted easier extraction. The pentane solution was washed with water to neutrality, was dried over calcium chloride, and was distilled in a small Claisen flask. Water-white distillate (2.9 g. or 71%), b.p. 85° (25 mm.), $n^{25}\text{D}$ 1.49194 and density (25°) 0.8132 was taken as nonadien-1,2-yne-4.

Anal. Calcd. for C_9H_{12}: C, 89.94; H, 10.06; active hydrogen, 0.0%; *MR*, calcd. by adding 1 unit for conjugation[20] and 0.44 unit for allenic grouping to the bond values,[21] 42.58. Found: C, 89.55; H, 10.20; active hydrogen (with either lithium aluminum hydride or methylmagnesium iodide), 0.0%; *MR*, 42.87.

An attempted determination (micro) of the normal boiling point resulted only in polymerization of the sample.

The ultraviolet absorption curve (Fig. 2) taken with 6.58 × 10^{-5} *M* solution in 95% alcohol shows a single maximum at 220.5 mμ with ε in the order of 8.2 × 10^3. The infrared spectrum (Fig. 1) has no peak at 3.03 μ (3300 cm.$^{-1}$). Allenic absorption is present at 5.15 μ (1942 cm.$^{-1}$) as well as at 5.86 μ (1710 cm.$^{-1}$) and 11.71 μ (853 cm.$^{-1}$). A minor but presumably significant peak at 4.91 μ (2039 cm.$^{-1}$) is taken to indicate the presence of some nonadiyne-2,4. The C≡C stretching absorption is observed at 4.48 μ (2230 cm.$^{-1}$) with a shoulder resolvable in the Perkin–Elmer spectrophotometer to a weak peak at 4.52 μ (2210 cm.$^{-1}$).

Ozonolysis of Nonadien-1,2-yne-4.—Ozonized oxygen was bubbled through a solution of nonadien-1,2-yne-4 (0.819 g. or 0.0068 mole) in methylene chloride (50 ml.) at 0°. Of the 10.2 millimoles of ozone introduced during the course of 64 minutes, 8.9 millimoles was absorbed. The reaction mixture was treated with water (50 ml.) and boiled on the steam-bath for 5 minutes (some material was lost here by accident). After extraction of the cooled mixture with ether, the acid product was transferred from the ether to bicarbonate solution, and then back to ether. Distillation afforded 0.087 g. (12%) of a faintly yellow liquid with the smell of valeric acid, and with b.p. (micro) 182°. The redistilled acid (neutralization equivalent of 112 as against 102 for valeric acid) furnished a *p*-phenylphenacyl ester, m.p. 67.5–68°. The melting point of this material admixed with authentic *p*-phenylphenacyl valerate, m.p. 67–68.5°, was 68–68.5°.

Nonadiyne-2,4 (III).—1,4-Dichlorobutyne-2 was prepared according to Johnson[22] by the reaction of butyne-1,4-diol[18] with thionyl chloride. Treatment of the 1,4-dichlorobutyne-2 first with sodamide and then with butyl bromide gave octadiyne-1,3,[12] b.p. 67–68° (24 mm.), $n^{25}\text{D}$ 1.4693, which showed infrared absorption at 3.03 μ (3290 cm.$^{-1}$), 4.34 μ (2300 cm.$^{-1}$), 4.48 μ (2225 cm.$^{-1}$) and 4.84 μ (2065 cm.$^{-1}$).

Octadiyne-1,3 (10.6 g. or 0.10 mole) was added dropwise over a period of 30 minutes to a stirred mixture of sodamide in liquid ammonia prepared from 2.3 g. (0.10 g. atom) of clean sodium and 150 ml. of liquid ammonia. After an additional hour of stirring, 14.2 g. (0.10 mole) of methyl iodide was added during the course of 15 minutes. The mixture was allowed to reflux for 4 hours and then to evaporate overnight.

Ether (75 ml.) was added to the residue and the mixture was filtered. The solids were rinsed twice with ether, the combined ether portions were dried over magnesium sulfate, and were distilled at atmospheric pressure to remove solvent. The residue was distilled through a Claisen head to furnish nonadiyne-2,4 (7.36 g. or 71%), b.p. 87–92° (30 mm.), $n^{25}\text{D}$ 1.4905. As shown by a small absorption peak at 3.03 μ, this product contained traces of a terminal acetylenic compound, presumably octadiyne-1,3, which persisted even after two distillations. The impurity was removed by precipitation with copper in essentially the same manner as that used in the preparation of nonadien-1,2-yne-4. After distillation at b.p. 99–100° (37 mm.), the purified,

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(20) J. Cymerman-Craig, E. G. Davis and J. S. Lake, *J. Chem. Soc.* 1874 (1954).

(21) T. L. Jacobs and W. F. Brill, THIS JOURNAL, **75**, 1314 (1953).

(22) A. W. Johnson, *J. Chem. Soc.*, 1009 (1946).

water-white nonadiyne-2,4 showed $n^{25}D$ 1.49148 and density (25°) 0.8165. Molecular refraction: To the value calculated for nonadiyne-2,4,[19] 40.34, should be added the increment for diyne conjugation exaltation, which value however could not be located in the literature. The observed molecular refraction was 42.67.

Anal. Calcd. for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 90.29; H, 9.96.

The ultraviolet absorption curve (Fig. 2) taken with a 1.42 $\times 10^{-3}$ *M* solution in 95% alcohol, showed maxima at 224.5 mμ (ε 366), 232 mμ (ε 294), 237 mμ (ε 335) and 252 mμ (ε 194). The infrared absorption curve (Fig. 1) was free of maxima at 3.03 μ (terminal acetylene) and at 5.15 μ and 11.71 μ (terminal allene), but did show peaks at 4.42 μ (2260 cm.$^{-1}$), 4.56 μ (2190 cm.$^{-1}$), 4.65 μ (2150 cm.$^{-1}$) and at 4.91 μ (2039 cm.$^{-1}$).

Isomerization of Nonadiyne-1,4 Followed by Ultraviolet Absorption.—A solution containing freshly distilled allene-free nonadiyne-1,4 (10.07 mg.) and potassium hydroxide in 8:1 (vol.) alcohol-water (total volume 10 ml.) was held in a thermostated water-bath at 25°. The concentrations of nonadiyne-1,4 and of alkali were 8.39 $\times 10^{-3}$ *M* and 12.1 $\times 10^{-3}$ *M*, respectively. Samples were removed at intervals by pipet, drained into an equal volume of 0.0282 *N* sulfuric acid in alcohol water (8:1) and diluted with aqueous alcohol (1:1 vol.) so that the optical density at 220.5 mμ was 0.27–0.43. Readings were taken against a solution made up in the same manner as the sample but without the nonadiyne-1,4. The accompanying table shows how the density at 220.5 mμ rose rapidly and then fell slowly. At 10,000 minutes and 11,400 minutes, the ultraviolet curves began to take on the shape of the curve for nonadiyne-2,4. The ultraviolet curves of samples removed between 20,100 and 26,000 minutes showed maxima at 225 mμ (ε 370–425), 232 mμ (ε 310–360), 236–237 mμ (ε 340–390) and 252 mμ (ε 207–229). The isomerization of skipped diyne I to allene II is at least 18 times as fast as the isomerization of allene II to conjugated diyne III; this estimate was arrived at by taking the ratio of the time required for the optical density at 220.5 mμ to reach a maximum to the time required for this maximum to become small.

Time, min.	Optical density[a]	Time, min.	Optical density[a]
7.5	6[b]	1400	43
71	34[c]	1800	34
140	55	2900	20
320	74	5700	7[d]
420	71		

[a] Of original solution. [b] Shoulder at 220.5 mμ. [c] Maximum at 220.5 mμ. [d] No maximum at 220.5 mμ.

Isomerization of Nonadiyne-1,4 Followed by Infrared Absorption.—A solution made up of allene-free nonadiyne-1,4 (3.720 g. or 0.0309 mole), 5.00 ml. of 4.72 *N* aqueous sodium hydroxide and enough absolute alcohol to bring the volume to 50.00 ml. was kept in a water-bath at 25°. At intervals, 10-ml. samples were removed and were drained into 40 ml. of petroleum ether (30–60°) and 40 ml. of water. Each sample was worked up in the usual manner to give 0.52–0.60 g. of vacuum distilled material (70–80% recovery). A trial recovery experiment with nonadiyne-1,4 performed as above but without alkali showed that the recovery with or without alkali was approximately the same. The compositions of the samples, estimated from the intensities of absorptions at 3.03, 5.15 and 4.91 μ, are given in the accompanying table. The infrared absorption curves (Baird) of the 22-hour and of the 49-hour sample were substantially the same as that of nonadiyne-2,4 in Fig. 1. The ultraviolet absorption curve of the 49-hour sample showed maxima at 224.5 mμ (ε 406), 232 mμ (ε 232), 237 mμ (ε 350) and 252 mμ (ε 203). In another experiment in which nonadiyne-1,4 was isomerized to nonadiyne-2,4, the isomerized material showed absorption maxima at 224.5 mμ (ε 382), 232 mμ (ε 308), 237 mμ (ε 340) and 252 mμ (ε 203).

	Approximate per cent. of		
Hours	Nonadiyne-1,4	Nonadien-1,2-yne-4	Nonadiyne-2,4
0.0	100	0	0
0.5	<10	>40	40
1.25	<10	20–40	60– 80
3	0	<10	90–100
22	0	< 1	100
49	0	0	100

Isomerization of Nonadien-1,2-yne-4.—A reaction mixture made up of nonadien-1,2-yne-4 (1.533 g. or 0.0128 mole), 5.00 ml. of 4.72 *N* aqueous sodium hydroxide with enough absolute alcohol to bring the total volume to 50.00 ml. was thermostated at 25°; 17-ml. samples were removed at intervals, quenched in a mixture of 10% sulfuric acid (5 ml.), water and ice, extracted with pentane and worked up as usual. No absorption peak at 3.03 μ (terminal acetylene) appeared after 3, 21 or 45 minutes. Judging from the absorptions at 4.91 and 5.15 μ, very little change occurred after 3 minutes. At 45 minutes nonadiene-1,2-yne-4 and nonadiyne-2,4 were present in approximately equal amounts.

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The Polymerization of Ethylene by Lower Valent Compounds of Titanium

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Ethylene is polymerized at atmospheric pressure to a high molecular weight, linear polymer by the products obtained from the reaction of titanium tetrachloride with various organometallic alkylating agents. Rates of polymerization have been followed at constant temperature and pressure, and catalytic activity has been related to: (a) the titanium tetrachloride concentration, (b) the ethylene concentration, (c) the nature of the alkylating agent, (d) the alkylating agent-to-titanium tetrachloride mole ratio, and (e) the temperature of polymerization. The weight of polymer produced after a given length of time is directly proportional to the titanium tetrachloride and ethylene concentrations. Although there is usually a decrease in rate of polymerization during the reaction, catalytic activity remains constant under conditions where very low molecular weight, soluble polymer is produced. A mechanism which involves propagation by a lower valent alkyltitanium or alkyltitanium halide is proposed to explain these results.

Introduction

Numerous publications[1-3] have appeared recently describing the polymerization of ethylene to a high molecular weight, linear polymer by the reaction products of $TiCl_4$ and organometallic alkylating agents. Following the independent discovery in this Laboratory[4,5] that ethylene, α-

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(1) K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew. Chem.*, **67**, 541 (1955).

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(3) G. Natta, I. Pasquon and E. Giachetti, *Angew. Chem.*, **69**, 213 (1957).

(4) E. I. du Pont de Nemours & Co. British Patent 776,326 (June 5, 1957).

(5) A. W. Anderson and N. G. Merckling, U. S. Patent 2,721,189 (October 18, 1955).