g (69% yield). Per cent yield is based on the availability of Grignard reagent since 50.5 g of the Grignard dimer 11 was also isolated from this mixture. The purity of 12 was improved by distillation, bp 108° (1.2 mm), n^{25}D 1.4302.

Anal. Calcd for $C_{13}H_{26}O_2$: C, 72.84, H, 12.22. Found: C, 72.50; H, 12.01.

4,4-Dimethyl-1-nonanol (13).—Addition of an ethereal solution of 198 g (0.93 mol) of 12 to a stirred suspension of 33 g of lithium aluminum hydride in 1200 ml of ether, followed by the usual procedures, gave a total of 152 g (95%) of 13, bp 105–109° (1.0 mm). The purity of 13 was improved by distillation, bp 109° (1.0 mm), n^{25}D 4.4400.

Anal. Calcd for $C_{11}H_{24}O$: C, 76.67; H, 14.04. Found: C, 76.67; H, 14.17.

1-Bromo-4,4-dimethylnonane (14).—A mixture of 48% hydrobromic acid (384 g, 2.24 mol), concentrated sulfuric acid (98 g, 1 mol), and 13 (152 g, 0.88 mol) was refluxed for 5 hr at 125°. The cooled solution was diluted with water and filtered through Hyflo Super Cel; the bromide layer separated. The crude bromide was washed with 10 ml of cold sulfuric acid, 100 ml of water, and 100 ml of 10% sodium carbonate. Crude 14 was dried (MgSO₄), filtered, and distilled, bp 94° (1.0 mm), n^{25}D 1.4578, yield 75%.

Anal. Calcd for $C_{11}H_{23}Br$: C, 56.16; H, 9.85; Br, 33.97. Found: C, 56.03; H, 10.13; Br, 34.03.

6,6,11,11,17,17,22,22-Octamethylheptacosane (22b). A. Huang-Minlon Modification.—19b (20.0 g, 0.038 mol), 15 ml of 85% hydrazine hydrate, 200 ml of diethylene glycol, and potassium hydroxide (15 g, 0.27 mol) were refluxed for 16 hr at 155° before the heat was increased to 165° to collect 15 ml of low boiling components. The reaction mixture was heated at 195° for 4 hr, cooled, and diluted with ether and water; the ether extracts were collected and washed to neutrality. The dried ether extracts (MgSO₄) were concentrated on a steam bath and the residue was distilled under vacuum to yield five fractions. The highest boiling fraction, bp 195–215° (0.2 mm), was shown by glc to be mainly 22b (10.4 g) with minor impurities. Chromatography on alumina using heptane gave 6.0 g (32% yield) of 22b in high purity (>99%), bp 220° (0.2 mm).

B. Nagate and Itazaki Modification.—19b (22.6 g, 0.043 mol), 85% hydrazine hydrate (287 g, 5.57 mol), hydrazine dihydrochloride (73.0 g, 0.7 mol), and triethylene glycol (980 g, 6.5 mol) were heated for 12 hr at 130–150° with a Soxhlet extractor or apparatus containing calcium oxide (50 g) fitted to the reaction flask to remove traces of water. The reaction mixture was heated for an additional 12 hr until the temperature rose to 175° and cooled; after KOH (106 g, 1.9 mol) addition, it was then heated to 175° for 6 hr and finally to 225° for 4 hr. The cooled reaction mixture was worked up by the usual procedure and 13.5 g of a crude reaction product, bp 140–185° (0.07 mm), was obtained. Chromatography on alumina using heptane gave 7.5 g (35% yield) of 22b, bp 208° (0.1 mm), in high purity (>99%) as evidenced by glc analysis.

High Temperature Pyrolysis of C₁ to C₄ Hydrocarbons[1]

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The pyrolysis of nine hydrocarbons at 1200° has been studied. The main products, which were the same for all hydrocarbons studied, were 1,3-cyclopentadiene, benzene, toluene, phenylacetylene, styrene, indene, and naphthalene. Twenty-three minor products were identified. The distribution of products can be accounted for in terms of polymerization of acetylene, produced by the pyrolysis of the hydrocarbon, and the addition of CH₂ or CH₃ to some of the acetylene polymers.

Pyrolyses of simple hydrocarbons have been studied previously by various investigators with the main emphasis on the kinetics and mechanism of decomposition.[2–6] However, these pyrolyses were usually done at relatively low temperatures (500–700°) and only the main end products were analyzed, with a few exceptions.[7–11] We report here pyrolysis reactions that take place at higher temperature (1200°) with particular emphasis on the product analysis. We have attempted to describe the mechanism on the basis of the nature of the end products and their relative yields.

The pyrolysis chamber contained a hot tungsten wire, and the walls of the flask were kept cold so that high-molecular-weight compounds formed by a recombination of the initial fragmentation of the hydrocarbons were condensed on the walls of the chamber and were not subjected to further pyrolysis to a significant degree.[12,13] The major products from these pyrolyses are shown in Table I. The minor components are listed at the bottom of Figure 1 in order of their retention time on the gas chromatograph column.

Results and Discussion

The pyrolysis of each of the hydrocarbons studied at 1200° leads to the same end products, but both the

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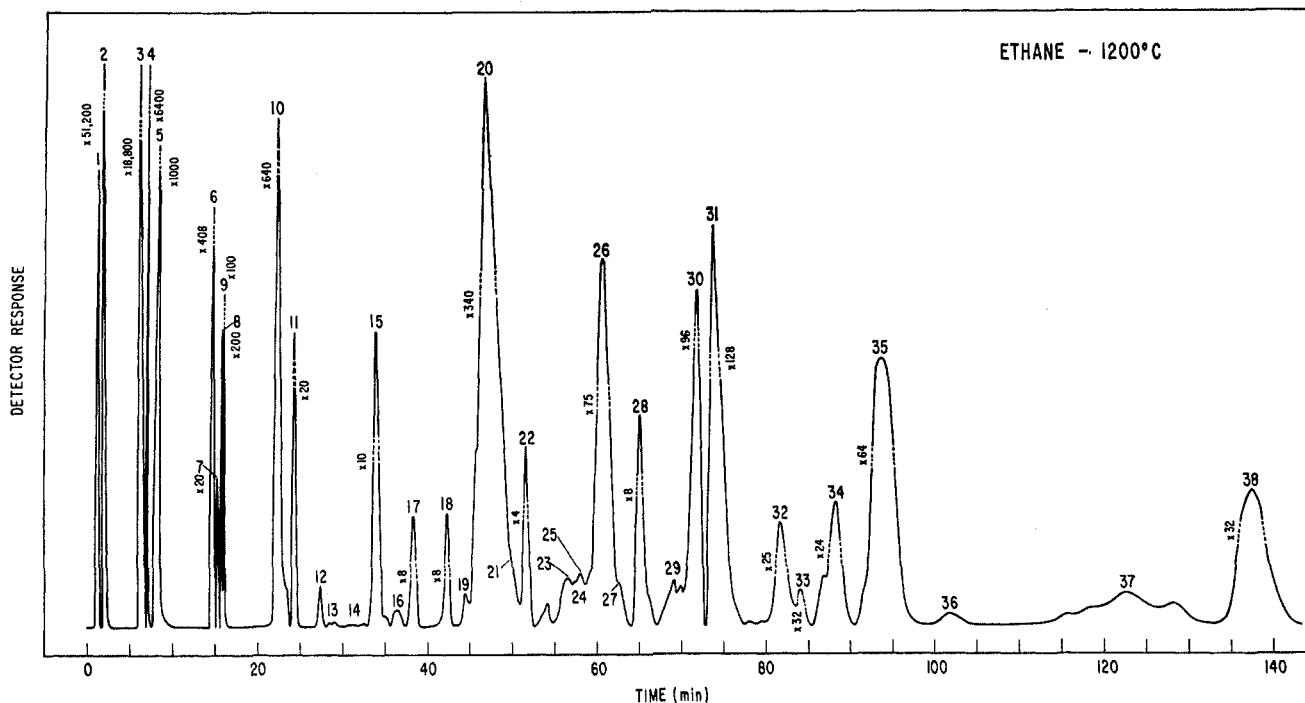(13) N. Friedmann and S. L. Miller, *Science*, **166**, 766 (1969).

Figure 1.—Gas chromatograph analysis of products from the pyrolysis of ethane at 1200°. Varian Model 1200 was used with 10-ft, $^1/_8$-in. stainless steel Porapak Q. The column temperature was programmed as follows: isothermal at 40° for 5 min, then 8° min^{-1} for 10 min followed by 2° min^{-1} to a temperature of 240° where it remained isothermal to the end of the run. Peaks 1–14 were analyzed with a sample of the gas phase and 15–38 with a sample of the liquid phase: (1) hydrogen; (2) methane; (3) ethylene; (4) acetylene; (5) ethane; (6) propene; (7) propane; (8) propyne; (9) allene; (10) 1,3-butadiene; (11) 1,3-butadiyne; (12) 2-butene; (13) 1-butene; (14) 3-pentene-1-yne; (15) 1,3-cyclopentadiene; (16) 2-pentyne; (17) *trans*-1-pentyne-3-ene; (18) methyldiacetylene; (19) 1,3,5-hexatriene; (20) benzene; (21) 1,3-cyclohexadiene; (22) three hydrocarbons (triacetylene? 1,5-diyne-3-hexene? 2-methylcyclopentadiene?); (23) methyl-1,3-cyclohexadiene; (24) 1-heptyne; (25) C₇H₁₀; (26) toluene; (27) C₇H₁₀; (28) 1,3,5-cycloheptatriene; (29) four hydrocarbons with mol wt 112, 110, 108, 106; (30) phenylacetylene and ethylbenzene; (31) styrene; (32) α- or β-methylstyrene; (33) C₈-benzene (mol wt 120); (34) 2,3-dihydroindene; (35) indene; (36) 4-phenyl-1-butene; (37) 1-methylindene; (38) naphthalene.

TABLE I

MAJOR PRODUCTS FROM THE PYROLYSIS OF HYDROCARBONS AT 1200°

|	Benzene[a]	Toluene	Phenyl-acetylene	Styrene	Indene	Naphthalene	Cyclo-pentadiene
Methane	0.1	63	75	96	81	42	375
Ethane	18.4	31	20	35	21	8.1	1.3
Ethylene	22.8	16	5.2	24	18	2.0	4.2
Acetylene	42.3	3.5	15	10	13	8.0	0.1
Propane	15.2	22	3.5	8.2	3.1	1.6	3.6
Cyclopropane	5.3	15	2.0	4.9	0.9	Trace	14
Allene	19	11	2.1	3.1	0.8	0.7	6.9
Butane	12.1	15	5.4	10	7.0	Trace	11
Isobutane	13.2	24	8.7	13	15	6.3	0.5

[a] Per cent yield of benzene based on the total carbon initially present. The entries for the other compounds are the yields relative to benzene taken as 100. The pyrolyses lasted for 2 hr.

relative and absolute yields vary markedly (Table I). Benzene is the major end product for all the hydrocarbons pyrolyzed with the exception of methane, and the yield ranges from 5 to 43%. In the case of methane, not only is the absolute yield of benzene $^1/_{50}$th the yield from any of the other hydrocarbons, but benzene is not the major end product. The yield of 1,3-cyclopentadiene from the pyrolysis of methane is about four times as great as that of benzene.

The effect of changing the wire temperature was studied with the pyrolysis of ethane. Ethane was pyrolyzed for 2 hr at temperatures of 800, 1000, 1200, and 1400°; the yield of benzene based on the initial amount of ethane added was 0.09, 0.12, 18, and 25% respectively. The relative yields of other end products

at these different temperatures were nearly the same as the values at 1200° given in Table I.

The similarity of products and yields from the C₂, C₃, and C₄ hydrocarbons, as well as the different results with CH₄, can be explained on the basis that the reactive species in these pyrolyses is acetylene or an activated form of it. A consideration of such an intermediate explains first the relatively low yield of end products from the pyrolysis of methane compared with the yield from the other hydrocarbons. The products from methane, ethane, ethylene, and acetylene account for 0.8, 47, 38, and 63%, respectively, of the initial hydrocarbon added. Secondly, methane yields a ratio of C₂ₙ molecules to C₂ₙ₊₁ molecules less than unity (0.6), whereas for the other gases this ratio varies from 3.1 for

SCHEME I
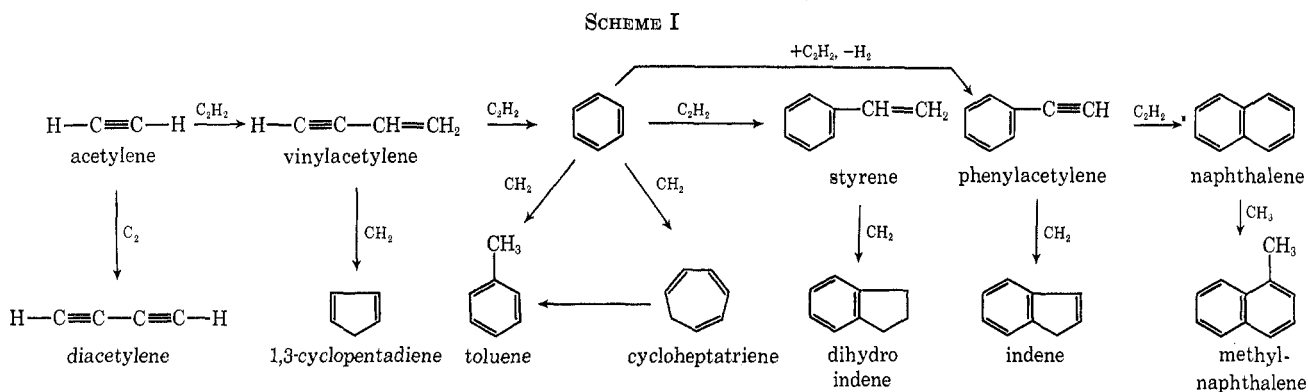
ethane to 7.8 for acetylene. Furthermore, since methane cannot undergo initial dehydrogenation to form the reactive C_2 intermediate, a recombination of the initial fragments (methyl radicals or carbene) must take place before any polymerization reaction proceeds. This explains the large yield of cyclopentadiene from the pyrolysis of methane. Once such a two-carbon reactive intermediate has been formed it is more likely to react with a one-carbon radical to form a C_3 molecule than to react with an acetylene. Since the walls of the pyrolyzing chamber are kept only at about $-30°$, a C_3 molecule will not condense on the walls and will be subject to further reactions such as two consecutive additions of a C_1 molecule to form 1,3-cyclopentadiene, which will largely condense on the $-30°$ walls.

The formation of cyclopentadiene, cycloheptatriene, toluene, dihydroindene, and indene can be accounted for by the reaction of CH_2 with even-carbon products of the pyrolysis (Scheme I). The reaction of CH_3 radicals instead of, or in addition to, the CH_2 could also account for the odd-carbon products. Carbene is known to react at lower temperatures with benzene[14,15] to give toluene and cycloheptatriene in a ratio of 1 to 3. The higher temperatures would isomerize most of the cycloheptatriene to toluene. That a one-carbon intermediate is available is also seen from the examination of *n*-butane and isobutane with respect to their yield of 1,3-cyclopentadiene. In the case of butane, once a one-carbon radical is formed it will react with the available parent compound or dehydrogenated products (*e.g.*, diacetylene, vinylacetylene, etc.) to form large quantities of 1,3-cyclopentadiene after further dehydrogenation. In the case of isobutane this is not possible due to the presence of the secondary carbon in the parent compound, and so the yield of 1,3-cyclopentadiene is relatively low.

Pyrolyses at temperatures lower than studied here give more highly hydrogenated products and the reaction mechanism probably involves radical intermediates formed by breaking a single bond. At temperatures above 1000°, acetylene is more stable than ethylene, ethane, or higher hydrocarbons. Rate of bond breaking at 1200° is sufficiently rapid that more than one bond can be broken during the pyrolysis. Therefore, the character of the high temperature pyrolysis is different from those at temperatures between 400 and 700° and appears to be dominated by acetylene polymerizations.

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We have previously shown the role of phenylacetylene in the synthesis of phenylalanine and tyrosine under primitive earth conditions.[13] The other hydrocarbons reported here from pyrolysis reactions may be useful starting materials for other prebiotic synthesis reactions.

Experimental Section

Materials.—Methane, pure grade, was obtained from Phillip's Petroleum Co. Lecture bottles of ethane, ethylene, propane, allene, cyclopropane, butane, and isobutane were obtained from Matheson Co. and were used without further purification. Acetylene was synthesized from calcium carbide and purified on a vacuum line directly before use.

Pyrolysis.—The hydrocarbons were introduced to the pyrolyzing vessel through a vacuum line. The reaction chamber consisted of a 1-l. flask in which a 0.025×15 cm tungsten wire was connected between two tungsten electrodes which in turn were connected to an Electro D.C. Power Supply Model NFB. The flask was immersed in an ethanol bath maintained between -35 and $-20°$ by adding Dry Ice. The tungsten wire was heated to temperatures between 800 and 1400° for 2 hr. The temperature of the wire was measured using a Pyrometer Instrument Co. Model 95. When the reaction was completed the flask was cooled to $-78°$, and the products volatile at this temperature were saved for analysis. The vessel was then brought to room temperature and the visible liquid at the bottom was distilled overnight into a tube cooled with Dry Ice. The distillation was completed by heating the reaction vessel to 100°. This distilled material was weighed and then sealed in a tube until used for analysis.

Identification: Benzene, toluene, phenylacetylene, styrene, and indene were identified by their retention time on two gas chromatograph columns, and by their ir and uv spectra. The columns were 5-ft 0.25-in. aluminum tubing containing 20% DEGS on Chromosorb P, and 5-ft $^1/_8$-in. stainless steel tubing containing Porapak Q. The unknown peaks were collected at the column exit. The infrared and ultraviolet spectra were obtained using Perkin-Elmer Infracord and Cary Model 15 spectrophotometers.

The other hydrocarbons were identified by combined gas chromatography and mass spectrometry. The gas chromatograph was a Varian Aerograph Model 1200 and a flame ionization detector. The mass spectrometer was a Hitachi Perkin-Elmer Model RMU-6D single focusing instrument. A 10-ft $^1/_8$-in. stainless steel Porapak Q column was used for the separation. A 4-to-1 splitter divided the column effluent so that 80% of the sample went to the flame ionization detector and 20% went to the mass spectrometer inlet system. A Watson–Biemann helium separator served to enrich the sample and reduce the pressure at the mass spectrometer inlet.[16]

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