to give the following fractions at 2 mm.; b.p. 25–158°, 1.17 g.; b.p. 158–160°, 8.17 g. (58%), $n^{25}D$ 1.4723. A small sample of the latter fraction was redistilled for analysis, $n^{25}D$ 1.4718.

Anal. Calcd. for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10. Found: C, 75.71; H, 7.87.

5-Undecynedioic Acid.—A solution of 8.17 g. (0.0469 mole) of 1,9-dicyano-4-nonyne in 56 ml. of ethanol and 14 ml. of water containing 10.5 g. of potassium hydroxide was refluxed for 10 hours. Ethanol (22 ml.) was allowed to evaporate, and the solution was cooled and made strongly acidic with concentrated hydrochloric acid. The product that separated was collected, dried and recrystallized from benzene; 7.92 g. (80%), m.p. 78–79°. A sample for analysis was recrystallized four times from ether–pentane; m.p. 79.5–81°.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.09; H, 7.51.

Dimethyl 5-undecynedioate was prepared in the usual way in 89% yield from 5-undecyne-1,11-dioic acid, methanol and sulfuric acid catalyst; b.p. 150–151° (5.5 mm.), $n^{25}D$ 1.4578.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.89; H, 8.39. Found: C, 64.76; H, 8.18.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO UNIVERSITY, ATHENS, O.]

Reactions of Diolefins at High Temperatures. III. Reversible Dissociation of 1,5-Alkadienes and Sensitization of Cyclization by Allyl Bromide[1,2]

BY WILLIAM D. HUNTSMAN

RECEIVED JULY 7, 1960

The behavior of several simple 1,5-alkadienes at 460° has been investigated. 2-Methyl-1,5-hexadiene yields 1,5-hexadiene and 2,5-dimethyl-1,5-hexadiene; the reversibility of this reaction was demonstrated by pyrolyzing an equimolar mixture of 1,5-hexadiene and 2,5-dimethyl-1,5-hexadiene whereupon 2-methyl-1,5-hexadiene was formed. The product from 1,5-heptadiene contains 1,5-hexadiene, 3-methyl-1,5-hexadiene, 3-methyl-1,5-heptadiene and 1,5-heptadiene; a mixture very similar in composition is obtained from 3-methyl-1,5-hexadiene. These reactions are rationalized in terms of a reversible dissociation mechanism involving allylic free radicals. Small amounts (*ca.* 1%) of allyl bromide sensitize the formation of cyclic products from 1,5-diolefins at 460°. For example, cyclohexene and benzene are obtained from 1,5-hexadiene, while benzene, toluene, vinylcyclopentane, and 1-, 3- and 4-methylcyclohexene are formed from both 1,5-heptadiene and 3-methyl-1,5-hexadiene. A free radical chain mechanism is believed to operate in the cyclization reaction.

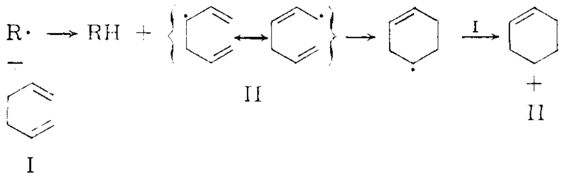
Introduction

Although the behavior of 1,5-hexadiene at high temperatures has been carefully studied, little work has been reported on the higher 1,5-alkadienes. In this paper the results of a study of some simple 1,5-alkadienes are reported.

The primary step in the thermal decomposition of 1,5-hexadiene appears to be the formation of allyl free radicals by homolytic cleavage of the central carbon–carbon bond; abstraction of hydrogen atoms from 1,5-hexadiene or other hydrogen donors by the allyl radicals leads to propylene, the major pyrolysis product.[3] Indeed the presence of allyl radicals during the pyrolysis of 1,5-hexadiene has been demonstrated by mass spectrometry.[4] Szwarc estimates the bond dissociation energy of the central bond in 1,5-hexadiene to be 38 kcal./mole, a value which is much lower than those found for simple alkanes.[5] It is generally agreed that the weakening of this bond is due to the high degree of resonance stabilization of the allyl radical.

It has also been demonstrated that allyl radicals, generated by the pyrolysis of allyl halides and other derivatives, may recombine to give 1,5-diolefins. For example, allyl radicals and 1,5-hexadiene were detected mass spectrometrically during the pyrolysis of allyl iodide,[4] and in the same way, β-methylallyl radicals and 2,5-dimethyl-1,5-hexadiene were shown to be formed by the pyrolysis of β-methylallyl iodide.[6] The formation of 1,5-hexadiene by the pyrolysis of 4-phenyl-1-butene apparently involves the dimerization of allyl radicals.[7]

Substantial amounts of cyclohexene and benzene are formed by the pyrolysis of 1,5-hexadiene at 540°, and it has been postulated that hexadienyl radicals (II), formed from 1,5-hexadiene through hydrogen abstraction, are forerunners of cyclization as illustrated by eq. 1.



(1)

Another type of thermal reaction—the Cope rearrangement—occurs at temperatures considerably below those at which dissociation occurs.[8] For example, the interconversion of 1,5-heptadiene and 3-methyl-1,5-hexadiene occurs slowly at 300° by an intramolecular mechanism.

Results and Discussion

Reversible Dissociation.—The product obtained by pyrolysis of 2-methyl-1,5-hexadiene (III) at 460° consisted largely of unchanged (III) along with smaller amounts of 1,5-hexadiene (I) and 2,5-dimethyl-1,5-hexadiene (IV). From an experiment in which the contact time was 21 seconds, the liquid product contained 4% (I) and 3% (IV);

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(1) Paper II of this series: W. D. Huntsman, V. C. Solomon and D. Eros, THIS JOURNAL, **80**, 5455 (1958).

(2) This research was supported by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command under contract No. AF18(600)546. The author acknowledges with gratitude the financial aid provided by the National Science Foundation for the purchase of the Perkin-Elmer model 21 infrared spectrophotometer used in this study (NSF-G3912).

(3) C. D. Hurd and H. T. Bollman, *ibid.*, **55**, 699 (1933).

(4) F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).

(5) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

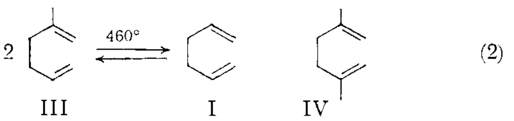
(6) C. A. McDowell, F. P. Lossing, I. H. S. Henderson and J. B. Farmer, *Can. J. Chem.*, **34**, 345 (1956).

(7) L. M. Porter and F. F. Rust, THIS JOURNAL, **78**, 5571 (1956).

(8) H. Levy and A. C. Cope, *ibid.*, **66**, 1684 (1944).

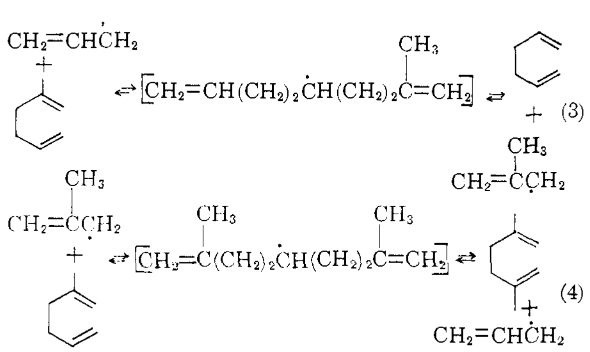
upon increasing the contact time to 43 seconds, the amounts of I and IV increased to 7 and 8%, respectively.[9] When an equimolar mixture of I and IV was heated at the same temperature with a contact time of 63 seconds, the product contained approximately 20% (III).

These reactions, as summarized in eq. 2, can be interpreted most readily by assuming scission of the central



III I IV (2)

carbon–carbon bond in the dienes followed by scrambling during the recombination of the allyl and β-methylallyl radicals. An addition–elimination process of the type illustrated by 3 and 4 is also possible and reasonable. In fact, in the pyrolysis



$$\mathrm{CH_2{=}CH\dot{C}H_2} + \;\rightleftarrows \left[\mathrm{CH_2{=}CH(CH_2)_2\dot{C}H(CH_2)_2\overset{\overset{\textstyle CH_3}{|}}{C}{=}CH_2}\right] \rightleftarrows \; + \; \mathrm{CH_2{=}\overset{\overset{\textstyle CH_3}{|}}{C}\dot{C}H_2} \quad (3)$$

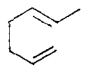
$$\mathrm{CH_2{=}\overset{\overset{\textstyle CH_3}{|}}{C}\dot{C}H_2} + \;\rightleftarrows \left[\mathrm{CH_2{=}\overset{\overset{\textstyle CH_3}{|}}{C}(CH_2)_2\dot{C}H(CH_2)_2\overset{\overset{\textstyle CH_3}{|}}{C}{=}CH_2}\right] \rightleftarrows \; + \; \mathrm{CH_2{=}CH\dot{C}H_2} \quad (4)$$

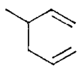
of allyl iodide, kinetic evidence favors this type of mechanism rather than the dimerization of allyl radicals for the formation of 1,5-hexadiene.[5]

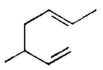
Relatively small amounts of high boiling material and gaseous products, principally propylene and isobutylene, were formed in these reactions. Careful analysis of the liquid products by gas chromatography revealed that no more than slight traces (less than 0.5%) of toluene and the methylcyclohexenes were formed from III; similarly, only traces of cyclohexene were formed from I. Evidently the cyclization reaction which has been observed to occur with I at 540°[7] does not occur at an appreciable rate at 460° with these compounds. On the basis of results described below, it appears that this is due to the inefficiency of hydrogen abstraction by the allyl and β-methylallyl radicals, *i.e.*, the first step in eq. 1, at the lower temperature. McNesby and Gordon have found that allyl radicals abstract hydrogen atoms very slowly at 400°, but quite rapidly at 500°.[10]

The behavior of 1,5-heptadiene (V) at 460° was similar to that observed with I, III and IV. The liquid product from an experiment in which the contact time was 58 seconds contained 14% 1,5-hexadiene (I), 10% 3-methyl-1,5-hexadiene (VI), 49% 1,5-heptadiene (V) and 4% 3-methyl-1,5-heptadiene (VII).[9] Several low-boiling cracking products (12%) and two other unidentified compounds (11%) as revealed by gas chromatography constituted the remainder. Compounds I, VI and VII are undoubtedly formed by the same mechanism as discussed above. By virtue of the unsymmetrical nature of the butenyl radical VIII, one would anticipate the formation of both V and VI from union with allyl radicals.[11] On the same basis one would expect some 2,6-octadiene (IX) and 3,4-dimethyl-1,5-hexadiene (X) to be formed in addition to VII by the union of two butenyl radicals, but this was not established because of the lack of pure samples of these compounds for comparison purposes.

Since allyl and butenyl radicals would also be expected to arise by dissociation of 3-methyl-1,5-hexadiene (VI), one would anticipate the same spectrum of products from this hydrocarbon as from 1,5-heptadiene (V). This was verified experimentally. The liquid product from the pyrolysis of 3-methyl-1,5-hexadiene (VI) with a contact time of 60 seconds contained 12% 1,5-hexadiene (I), 10% 3-methyl-1,5-hexadiene (VI), 56% 1,5-heptadiene (V), 5% 3-methyl-1,5-heptadiene (VII), 8% cracking products and three other unidentified compounds (9%).[9] Evidently extensive dissociation occurred, and it is interesting to note that the ratio of 1,5-heptadiene (V) to 3-methyl-1,5-hexadiene (VI) is roughly the same in this product as in the pyrolysate from 1,5-heptadiene (V). This probably corresponds to the equilibrium ratio of these hydrocarbons at 460°. Less than 0.5% toluene and methylcyclohexenes were formed during the pyrolysis of 1,5-heptadiene and 3-methyl-1,5-hexadiene.

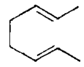

V

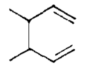

VI


VII

$[\mathrm{CH_3CH{=}CH\dot{C}H_2} \longleftrightarrow \mathrm{CH_3\dot{C}HCH{=}CH_2}]$

VIII


IX


X

A shoulder appeared on the trailing edge of the 1,5-heptadiene peak in the gas chromatography tracings of these pyrolysates, and it was also observed for the 1,5-heptadiene isolated by careful fractional distillation of the product from V. It is believed that this is due to an increased proportion of *cis*-1,5-heptadiene in the material recovered from pyrolysis. Whereas the infrared spectrum of the starting material exhibited weak absorption at 14.25 μ, indicative of a relatively small amount of the *cis* isomer, the spectrum of the 1,5-heptadiene isolated after pyrolysis showed a strong band at this same position. In all other regions, the spectra coincided except for minor differences in band intensities. From thermodynamic considerations one would anticipate an increased proportion of the *cis* isomer at equilibrium at high temperatures, since the conversion of *trans* to *cis*-isomer is undoubtedly endothermic.

Sensitized Cyclization.—In the early phases of this study, the 1,5-heptadiene used for pyrolysis was synthesized by conventional methods and

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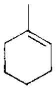
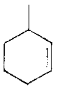
[9] Throughout this paper, composition data refer to the monomeric material obtained by distillation of the pyrolysates.

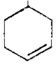
[10] J. R. McNesby and A. S. Gordon, THIS JOURNAL, 79, 4593 (1957).

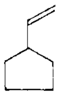
[11] It is conceivable, of course, that VI is formed from V by the Cope rearrangement, but it seems more likely that dissociation into radicals occurs at the temperature used.

purified by fractional distillation through a 90-cm. column packed with glass helices. The behavior of this material was remarkably different from that described above. Extensive decomposition, charring, and gas formation occurred, suggesting free radical chain processes. The liquid product was an exceedingly complex mixture, and no single compound could be isolated in a state of purity by fractional distillation. Through a combination of gas chromatography and infrared spectral analysis of the various cuts obtained by fractional distillation, however, compounds I, V, VI, VII and XI–XVI were identified. In addition, the gas chromatography tracing indicated the presence of cyclohexene, but this was not definitely established. Also, a small amount of a conjugated diolefin (λ_{max} 227 mμ) was present. Positive identification of this hydrocarbon was not possible, but it is believed to be 2,4-hexadiene on the basis of λ_{max} and the boiling range (78–84°) of the fraction in which it was concentrated. 2,4-Hexadiene has b.p. 82° and λ_{max} 227 mμ[12,13]

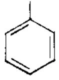

XI


XII


XIII


XIV

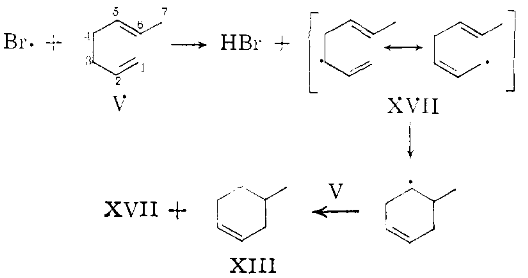

XV


XVI

The same spectrum of products in roughly the same proportions was obtained by pyrolysis of 3-methyl-1,5-hexadiene (VI) which had also been purified by careful fractional distillation. Originally the possibility was entertained that the formation of cyclic products from V and VI was due to an enhanced reactivity of the butenyl radicals formed by dissociation of these hydrocarbons. However, a comparison of the heats of formation of the allyl, β-methylallyl and butenyl radicals, 32, 21 and 26 kcal./mole,[6] respectively, argues against this possibility. Pyrolysis of a mixture of 1,5-hexadiene and 3-methyl-1,5-hexadiene (3:1 mole ratio) served to establish that there is no intrinsic difference in cyclization tendencies of these hydrocarbons, because a considerable quantity (18%) of cyclohexene was formed by cyclization of the 1,5-hexadiene. There remained then the possibility that a small amount of an impurity in V and VI was responsible for initiating the cyclization reactions; this was indeed found to be the case. Gas chromatography revealed the presence of a contaminant present to the extent of 0.5–0.7% in each hydrocarbon. Since allylic halides from which these hydrocarbons had been synthesized were the most likely contaminants, an experiment was carried out in which 1,5-hexadiene containing 1.4 mole % of allyl bromide was pyrolyzed. The reaction exhibited the characteristics of a free radical chain reaction, and the product was found to contain 34% cyclohexene and 9% benzene. Samples of V and VI were then treated with sodium in liquid ammonia to remove contaminating halides, and the material purified in this way underwent the simple reversible dissociation reactions upon pyrolysis as described above.

Pyrolysis of 1,5-heptadiene to which 1.4 mole % of allyl bromide had been added, gave a product containing 34% methylcyclohexenes, 11% toluene and 14% benzene. A small amount of vinylcyclopentane may also have been present, but this was not definitely established. 1,5-Hexadiene was not detected among the reaction products.

A free radical chain mechanism of the type suggested by Porter and Rust[7] seems most plausible for the formation of the cyclic olefins. Bromine atoms, formed by dissociation of allylic bromides, are the most logical choice as chain initiators. The formation of 4-methylcyclohexene (XIII) from 1,5-heptadiene (V) can be rationalized according to the following scheme. In a similar fashion, chains initiated by abstraction of a hydrogen atom from position 4 or 7 would lead ultimately to 3-methylcyclohexene (XII) and vinylcyclopentane (XIV), respectively. Abstraction of allylic hydrogens from 3-methyl-1,5-hexadiene (VI), formed from 1,5-heptadiene (V) by the reversible dissociation process, would lead to XI and XII.



The mode of formation of benzene and toluene is uncertain, but cyclohexadiene and the methylcyclohexadienes, formed by disproportionation of the free radicals antecedent to the cycloalkenes, are the most likely precursors. It is significant to note, however, that the product obtained by pyrolysis of a mixture of cyclohexene and 5 mole % allyl bromide contained only 1.7% benzene.

Experimental

Materials.—The diolefins used in this study were prepared by methods previously described and were purified by fractional distillation through a 90-cm. column packed with $^1/_8$-in. glass helices. The 1,5-heptadiene and 3-methyl-1,5-hexadiene used in runs 4, 6, and 7 were treated with sodium in liquid ammonia by the procedure of Young, Roberts and Wax for the removal of traces of halides.[14] The following constants were observed: 1,5-hexadiene,[15] b.p. 59–60°, n^{25}D 1.4012; 2-methyl-1,5-hexadiene,[16] b.p. 88–89°, n^{25}D 1.4155; 2,5-dimethyl-1,5-hexadiene,[17] b.p. 112–114°, n^{25}D, 1.4270; 1,5-heptadiene,[8] b.p. 93–94°, n^{25}D 1.4170; 3-methyl-1,5-hexadiene, b.p. 80–81°, n^{25}D 1.4079.

In addition to these diolefins, the following compounds were prepared as reference compounds for gas chromatography and infrared spectral analysis.[18]

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(12) A. L. Henne and A. Turk, THIS JOURNAL, **64**, 826 (1942).

(13) H. Booker, L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 1453 (1940).

(14) W. G. Young, J. D. Roberts and H. Wax, THIS JOURNAL, **67**, 841 (1945).

(15) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., (1955), p. 121.

(16) A. L. Henne, H. H. Chanan and A. Turk, THIS JOURNAL, **63**, 3474 (1941).

(17) S. H. Harper, H. W. B. Reed and R. A. Thompson, *J. Sci. Food Agric.*, **2**, 94 (1951).

(18) 3-Methylcyclohexene was identified only by comparison of infrared spectra with the recorded spectrum of this compound: Catalog of Infrared Spectral Data, Serial No. 898, American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., 1949.

TABLE I

PYROLYSIS EXPERIMENTS

Run	Hydrocarbon Kind	Wt., g.	Contact time, sec.	Product Volatile, g.	Polymeric, g.	Condensable gas, ml.
1	2-Methyl-1,5-hexadiene	10.27	21	8.84	0.80	65
2	2-Methyl-1,5-hexadiene	5.10	43	3.59	0.60	75
3	1,5-Hexadiene and 2,5-dimethyl-1,5-hexadiene	4.64 6.20	63	6.10	0.70	..
4	1,5-Heptadiene[d]	7.25	58	5.10	1.00	90
5	1,5-Heptadiene[a]	14.30	..[b]	5.21	1.92	1700
6	1,5-Heptadiene[c,d]	6.75	..[b]	3.00	1.10	900
7	3-Methyl-1,5-hexadiene[d]	6.00	60	3.75	1.15	120
8	3-Methyl-1,5-hexadiene[a]	11.82	..[b]	4.60	2.21	1250
9	1,5-Hexadiene	8.55	50	6.00	1.20	80
10	1,5-Hexadiene[e]	7.01	..[b]	3.25	1.05	..

[a] Hydrocarbon had been purified by fractional distillation; gas chromatography indicated the presence of 0.5–0.7% impurity. [b] Contact time could not be calculated because of the large volume of gas evolved during the pyrolysis. [c] Allyl bromide, 0.123 g., was mixed with the 1,5-heptadiene. [d] Purified by treatment with sodium in liquid ammonia. [e] Allyl bromide, 0.146 g., was mixed with the 1,5-hexadiene.

1-Methylcyclohexene.—The iodine-catalyzed dehydration of 1-methylcyclohexanol described by Mosher was used.[19] The product was fractionated through a 60-cm. column, b.p. 108–109°, $n^{25}\mathrm{D}$ 1.4478. Gas chromatography revealed the presence of 4% of an impurity, probably methylenecyclohexane.

4-Methylcyclohexene.—4-Methylcyclohexyl acetate was pyrolyzed at 470° by the usual procedure; the product had b.p. 102–103°, $n^{25}\mathrm{D}$ 1.4380.

Vinylcyclopentane.—1-Cyclopentylethyl acetate was pyrolyzed at 450°. Upon fractionation in a spinning band column, vinylcyclopentane, b.p. 97.9–98.2°, $n^{25}\mathrm{D}$ 1.4339, was obtained. A small amount of ethylidenecyclopentane was also formed during the pyrolysis.

3-Methyl-1,5-heptadiene was formed as a by-product in the synthesis of 3-methyl-1,5-hexadiene, and was isolated by fractionation of the high boiling material from the synthesis in a Podbielniak MiniCal column, b.p. 109.5–110°.

Pyrolysis Apparatus.—The pyrolyses were carried out in the flow system previously described.[20] Oxygen-free nitrogen was used as the carrier gas. Liquid products were collected in an ice-cooled receiver, and condensable gases were collected in a Dry Ice-cooled trap which was attached to the liquid product receiver.

At the conclusion of each run, the weight of liquid product was determined; this material was then subjected to simple distillation to remove high-boiling polymers, and the distillate was subjected to further analysis as described below. The condensable gases were allowed to evaporate into a gas bottle and were analyzed by gas chromatography. The volumes reported have been corrected to standard conditions.

Product Analysis.—Gas chromatographic analyses were performed on a Perkin–Elmer model 154–C vapor fractometer, using the following columns which contained the stationary liquid phase (*ca.* 40%) supported on Fisher Columpak: 4-m. decyl phthalate; 4-m. tritolyl phosphate; and 12-m. β,β'-oxydipropionitrile. Infrared analyses were performed with a Perkin–Elmer model 21 spectrophotometer.

The procedure used for the analysis of the volatile liquid products from most of the pyrolyses was as follows. A sample was analyzed by gas chromatography, and if sufficiently good resolution was achieved, the approximate composition was calculated. The mixture was then fractionated in a spinning-band column, or a 60-cm. Podbielniak MiniCal column, and the fractions were subjected to infrared analysis and gas chromatography. In most cases the composition of the individual fractions was sufficiently simple to permit a reasonable estimate of the proportions of the components.

Pyrolysis Experiments.—The weights of hydrocarbons pyrolyzed, contact times, etc., are summarized in Table I and product analyses are given below. Percentage composition data are given in mole per cent, and unless stated otherwise, unidentified cracking products constitute the difference between 100% and the total of the figures given. All experiments were carried out at 460 ± 5°.

Run 1: 4% 1,5-hexadiene, 3% 2,5-dimethyl-1,5-hexadiene and 88% 2-methyl-1,5-hexadiene were found in the liquid product. Propylene and isobutylene, in nearly equimolar proportions, were the major components of the condensable gas.

Run 2: The liquid product contained 7% 1,5-hexadiene, 8% 2,5-dimethyl-1,5-hexadiene and 79% 2-methyl-1,5-hexadiene. Only slight wiggles occurred in the gas chromatography tracing at the times corresponding to the retention times of the methylcyclohexenes and toluene. Propylene and isobutylene were the major components of the condensable gas.

Run 3: Upon fractional distillation, 1.40 g. of 1,5-hexadiene, 1.20 g. of 2-methyl-1,5-hexadiene and 2.58 g. of 2,5-dimethyl-1,5-hexadiene were isolated.

Run 4: The liquid product contained 14% 1,5-hexadiene, 10% 3-methyl-1,5-hexadiene, 49% 1,5-heptadiene, 4% 3-methyl-1,5-heptadiene and 11% of an unidentified component. A shoulder which is believed to be due to *cis*-1,5-heptadiene appeared on the trailing edge of the 1,5-heptadiene peak. The condensable gas consisted of 62% propylene, 12% 1-butene, 10% *trans*-2-butene, 10% *cis*-2-butene and 6% 1,3-butadiene.

Run 5: The product from this experiment was exceedingly complex and the analytical data are only approximate: 7% 1,5-hexadiene, 7% 3-methyl-1,5-hexadiene, 20% 1,5-heptadiene, 28% 1-,2- and 3-methylcyclohexenes, 5% vinylcyclopentane, and 2% 3-methyl-1,5-heptadiene. Gas chromatography indicated the presence of a small amount of cyclohexene but conclusive identification was not possible.

Run 6: The approximate composition of the liquid product was: 15% 1,5-heptadiene, 14% benzene, 34% 1-, 2- and 3-methylcyclohexene and 11% toluene. Condensable gases were: 55% propylene, 15% 1-butene, 16% *trans*-2-butene, 9% *cis*-2-butene and 5% 1,3-butadiene.

Run 7: The liquid product contained 12% 1,5-hexadiene, 10% 3-methyl-1,5-hexadiene, 56% 1,5-heptadiene and 5% 3-methyl-1,5-heptadiene. The composition of the condensable gas was essentially the same as in run 6.

Run 8: Approximately the same composition was found for the liquid product and the condensable gas as in run 6.

Run 9: Only a trace (1%) of cyclohexene was present in the liquid product; the remainder was 1,5-hexadiene along with a small amount of cracking products.

Run 10: 25% 1,5-hexadiene, 34% cyclohexene and 9% benzene were present. The ultraviolet spectrum showed $\lambda_{\max}$ 226 mμ, absorbance 0.370 (c 2.45×10^{-4} mole/liter, EtOH).

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