[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Pyrolysis of Alpha Unsaturated Hydrocarbons[1]

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To extend our knowledge of the pyrolysis of olefins beyond the C_5 members, these unsaturated hydrocarbons were chosen for study: diallyl, 4-methyl-1-pentene, allylcyclohexane and 4-phenyl-1-butene. All possess the general structure $R—CH_2CH{=}CH_2$, wherein R is a radical of low electron attraction. In contrast to propylene and isobutylene,[4] which required temperatures of 700° or above for extensive decomposition, these olefins decomposed considerably in the 425–500° range. Both types possess a $C\overset{\alpha}{—}C{=}C$ skeleton but the former has no $C\overset{\beta}{—}C\overset{\alpha}{—}C{=}C$ skeleton. This difference suggests that pyrolysis produces a rupture of the $C\overset{\beta}{—}C$ bond more readily than the $C\overset{\alpha}{—}C$.

Confirmation was found in the fact that propylene predominated throughout in the gases. The ethylene content was small, indicating an inconsiderable $C\overset{\alpha}{—}C$ scission. Saturated hydrocarbons and hydrogen comprised most of the remainder of the gas. Allene was sought for but not found.

In the lower boiling liquid products, materials were encountered which possessed slightly higher distillation ranges than the original hydrocarbon. They gave higher n_D values and, in the case of the liquid from diallyl, showed a different behavior toward tetranitromethane reagent. These facts suggest the presence of isomeric unsaturated hydrocarbons (such as 1,4- or 2,4-hexadiene from diallyl; 4-phenyl-2-butene from 4-phenyl-1-butene; etc.) or dehydrogenated compounds (such as 1,3,5-hexatriene from diallyl; phenylbutadiene or naphthalene from 4-phenyl-1-butene; etc.). Naphthalene was isolated in quantity from the phenylbutene liquids.

To compensate for the propylene found in the gas, much toluene (and some benzene) was formed from the phenylbutene. Similarly, cyclohexane, benzene and cyclohexene were indicated in the liquids from allylcyclohexane. Polymerization products were formed in every case, as shown by the high boiling material and tars which were encountered.

Mechanism.—The facts are best explained by assuming that these α-olefins undergo a preliminary scission into radicals at the allyl bond:

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(4) Hurd, Spence and Meinert, THIS JOURNAL, **51**, 3561 (1929); **52**, 4978 (1930).

$R—C_3H_5 \longrightarrow R— + C_3H_5—$. These radicals acquire hydrogen atoms from some source, presumably largely from the original hydrocarbon, and escape as $RH + C_3H_6$. The dehydrogenated material may escape as $R'CH{=}CH—CH{=}CH_2$ or, in common with the original unsaturated hydrocarbon, it may undergo polymerization.

The formation of propylene without allene from diallyl resembles the analogous formation of aniline without allene from allylaniline[5] and of methane without allene from isobutylene.[6] A compound analogous to diallyl, namely, tetraphenylhexadiene, $(Ph_2C{=}CH—CH_2—)_2$, has been reported[7] to pyrolyze into α,α-diphenylpropylene and tar. The tar was regarded as polymerized diphenylallene but this position now becomes untenable.

A conclusion may be drawn from the present work regarding the pyrolysis of hydrocarbons in general, namely, that simple scission into two compounds should not be considered the primary effect even though each of the two products may be among the products of the reaction (as in the case of ethane + ethylene, or methane + propylene, from *n*-butane).

Experimental Part

Preparation of Hydrocarbons.—The compounds studied were synthesized by the general method:[8] $RMgX + BrCH_2CH{=}CH_2 \longrightarrow RCH_2CH{=}CH_2 + MgBr$. In the synthesis of diallyl it was found convenient to use much less ether than Cortese recommended and to add the allyl bromide slowly. The *diallyl* used boiled at 58–60°. For the *allylcyclohexane*, b. p. 148–150°, these new constants were determined: d_4 = 20°/0.8160; 28.5°/0.8117; 41.5°/0.8010; n_D = 15°/1.4528; 25°/1.4483. The *dibromide of allylcyclohexane* gave these constants: b. p. 129–131 (11 mm.); n_D = 15°/1.5293, 20°/1.5271, 25°/1.5251. To synthesize *4-phenyl-1-butene*, benzylmagnesium chloride was used rather than the bromide. The hydrocarbon boiled at 175–178°; n^{20}_D 1.5090.

4-Methyl-1-pentene has not been made previously by this method. It was prepared from 24 g. of magnesium, 123 g. of isopropyl bromide in 150 cc. of dry ether, and 110 g. of allyl bromide in 250 cc. of ether. It was converted[9] (in ether solution) into the dibromide and the latter dehalogenated with zinc and alcohol. The weight of olefin, b. p. 52.5–54.5°, was 33 g. Based on the allyl bromide, this represents a 43% yield.

Method of Heating.—Except for the manner of introducing the liquid hydrocarbons at a uniform rate into the unpacked Pyrex reaction tube, namely, by displacement with mercury, the method of heating and of collecting the products was very similar to that described for isobutylene.[10] The data from some representative experiments are summarized in Table I.

In several experiments with diallyl, the gases were passed through bromine in carbon tetrachloride. In a typical case, 21.5 g. of liquid, b. p. 139–140°, n^{20}_D 1.5206, was formed. These data characterized the liquid as 90% propylene bromide and 10% ethylene bromide. There was about a gram of residue, 0.9 g. of which was butadiene tetrabromide, m. p. 114°. Allene tetrabromide was not formed.

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(5) Carnahan and Hurd, This Journal, **52**, 4586 (1930).

(6) Hurd and Spence, *ibid.*, **51**, 3568 (1928); Hurd and Meinert, *ibid.*, **52**, 4982 (1930).

(7) Wittig and Leo, *Ber.*, **63**, 943 (1930).

(8) Diallyl, Cortese, This Journal, **51**, 2267 (1929); allylcyclohexane, Resseguier, *Bull. soc. chim.*, [4] **7**, 431 (1910); 4-phenyl-1-butene, Lévy and Sfiras, *Compt. rend.*, **184**, 1335 (1927).

(9) Boord and co-workers, This Journal, **52**, 3396 (1930); **54**, 754 (1932).

(10) Hurd and Spence, *ibid.*, **51**, 3563 (1929).

TABLE I

PYROLYSIS OF FOUR UNSATURATED HYDROCARBONS

Temp., °C.	Vol. tube, cc.	Time, min.	Liq. used, g.	Products cond. by ice, g.	CO_2 used as diluent, cc.[c]	Contact time, sec.	Decomposition, %	Gas formed, cc.	Gaseous products, per cent. by volume						
									C_2H_2	Sol. in 62% H_2SO_4	C_3H_6	C_2H_4	H_2	C_nH_{2n+2}	n
Diallyl															
425	250	10	24.0	22.7	666	8	13	188	..	2.38	72.02	4.69	...	20.91	1.80
450	250	21	22.1	17.3	807	17	62	853	..	1.24	63.06	4.04	7.41	24.24	1.88
475	250	13	22.7	17.8	510	11	56	1308	3.25	5.29	63.65	4.01	4.01	19.78	1.84
500	520	8	22.5	16.1	594	13	66	2034	..	2.49	63.89	3.49	2.83	28.30	2.07
550	520	43	17.3	7.7	3909	52	91	4450	1.26	1.43	56.12	5.28	7.85	27.30	2.07
485	220[a]	15	21.9	16.6	2036	9	77	1517	0.57	2.28	61.92	3.63	9.33	22.26	1.55
650	17[b]	42	30.9	11.5	None	1.5	95	8698	..	0.60	48.60	9.90	10.40	30.50	1.49
4-Methyl-1-pentene															
600	250	50	28	7.9	None	31.4	73	4830	..	2.6	27.2	11.4	6.1	52.6	1.4
625	17[b]	108	23	7.1	None	5.5	87	8790	1.6	4.6	44.0	9.6	9.5	33.6	1.7
650	17[b]	101	25	6.2	None	4.6	95	10840	1.6	5.7	38.6	9.8	8.6	35.6	1.6
675	17[b]	74	28.8	5.9	None	2.8	96	12745	1.6	3.9	42.2	13.7	9.2	29.3	1.4
Allylcyclohexane															
500	17[b]	42	27.6	25.1	None	3.0	25	..	..	..	...	...	..	...	..
550	17[b]	105	38.0	17.0	None	5.2	75	6110	0.5	1.7	36.3	16.9	7.3	37.4	1.9
600	17[b]	89	42.3	18.4	None	3.7	85	9548	0.4	2.7	38.2	21.0	11.0	26.7	1.5
650	17[b]	57	36.5	14.0	None	2.6	90	12320	..	3.2	34.2	21.3	10.9	30.4	1.4
4-Phenyl-1-butene															
500	250	26	43.1	41.8	3910	12	27.5	610	..	3.5	74.6	4.7	7.6	9.6	2.3
500	250	76	46.9	44.4	5150	31	50	1260	..	1.1	59.7	10.6	10.5	18.1	2.0
550	250	57	49.7	43.3	1750	28	73	2530	..	1.2	46.8	10.0	15.9	26.1	1.7
600	250	13	28.2	22.9	482	12	88	2290	..	..	44.2	10.1	22.0	23.7	1.7
700	23	38	28.2	23.0	2770	2.3	77	2223	..	1.1	36.5	17.0	18.4	27.0	1.3

[a] Magnesium turnings in the tube about half filling the tube. [b] Quartz tube of small diameter used; Pyrex used elsewhere. [c] In experiments in which carbon dioxide was used, a steady flow of the gas was maintained throughout the experiment. This item was considered in calculating the contact time: Contact time = $(\text{vol. tube} \times \text{time in sec.} \times 273)/T^\circ$ Abs. $(((22400 \times \text{wt.})/\text{mol. wt.}) + \text{vol. } CO_2)$.

Some gas from a 500° run was cooled by liquid air. The condensate was distilled, the first fraction including everything from −190 to −80° (200 cc.) and the second from −80° to room temperature (300 cc.). Propylene, ethylene, methane and ethane (n in C_nH_{2n+2} was 1.23) were found in the first fraction. The last fraction contained much more propylene and a little ethane ($n = 2.04$). Propane and butane were not indicated.

A trace of butadiene (but no allene) was also found by brominating the gases from 4-methyl-1-pentene or allylcyclohexane. The saturated hydrocarbons from 4-methyl-1-pentene were methane and ethane. No liquid (propane or butane) condensed from it at −80°.

Liquid Products.—The extent of the decomposition was determined by distilling off the unused hydrocarbon from the condensed liquids. Obviously this method lacked the precision which was possible in work with gaseous hydrocarbons. From a 500° run with diallyl, the 16.1 g. of liquid gave these fractions: (°C., g, n_D^{22}) 58–60, 4.4, 1.406; 60–65, 3.7, 1.414; 65–75, 2.7, 1.440; above 75, 1.2, 1.465; and 4.2 g. of residue. In another run (485°), 8.97 g. in a 58–67° fraction was mixed with aniline and refractionated: (b. p., n_D^{20}) 58–60, 1.401; 60–63, 1.416; 63–69, 1.423. The 58–60° fraction was almost pure diallyl. A little of it, added to a mixture of 4 cc. of an ether solution of tetranitromethane and 2–3 drops of pyridine, caused no immediate coloration but in fifteen minutes a yellow-green color developed.[11] In contrast, the other fractions produced an almost immediate brown coloration. This may point to a conjugated hexadiene.

The high boiling residue from diallyl gave a solid, m. p. 47°, on bromination. Its bromine content was 66.3% and its molecular weight 476. This would be satisfactory for $C_{12}H_{20}Br_4$, $C_{12}H_{18}Br_4$ or $C_{12}H_{16}Br_4$.[12] The liquid and gaseous products were not markedly affected by the presence of magnesium[13] in the reaction tube.

Distillation of the liquids from allylcyclohexane gave volatile hydrocarbons (b. p. 70–145°), then recovered allylcyclohexane (145–150°), finally a tarry residue which was 4–5 times heavier than the volatile portion. The latter contained[14] aromatics, cycloalkanes and lesser amounts of cycloalkenes. The refractive index (20°) of the 78–85° fraction was 1.463, suggesting about equal parts of benzene and cyclohexene.

Fractionation of the liquids from the 550° run with 4-phenyl-1-butene gave 9.7 g. of benzene and toluene; 6 g. between 115–170°; 6.7 g., 170–178° (n_D^{20} 1.5225); 5 g., 178–185° (n_D^{20} 1.5268); 19.2 g. of residue about half of which was naphthalene. Some stilbene was also isolated from the residue. The 170–178° fraction contained the phenylbutene, but its high refractive index denoted a contaminant.

Summary

The pyrolysis of diallyl, 4-methyl-1-pentene, allylcyclohexane and 4-phenyl-1-butene was studied. All of these gave a predominating quantity of propylene as a gaseous product and none gave any allene. Liquid products were formed which pointed to isomerization, dehydrogenation and polymerization processes. A mechanism for these observations is outlined which also incorporates facts of other varied experiments on pyrolysis.

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[11] Werner, *Ber.*, **42**, 4324 (1909), observed a yellow coloration with amylene.

[12] Compare Lebedev, *J. Russ. Phys.-Chem. Soc.*, **45**, 1249 (1913), for diallyl polymers obtained by heating diallyl for ten hours at 250°.

[13] For its effect on the dry distillation of rubber, which also contains a —C═C—C—C—C═C— skeleton, see Midgley and Henne, THIS JOURNAL, **51**, 1285 (1929).

[14] The method of Egloff and Morrell [*Ind. Eng. Chem.*, **18**, 354 (1926)] was used.