CCLXXXVI.—*The Catalytic Hydrogenation of Different Types of Unsaturated Compounds. Part III. The Hydrogenation of Conjugated Systems.*

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IN Part II (this vol., p. 823) we classified conjugated systems according to their method of catalytic hydrogenation, and made a study of the hydrogenation of isoprene as being representative of Type II— the most complicated of the four types. It was also shown that a

diagram of the whole process could be constructed from a few suitably chosen experimental data. We have now studied three other compounds of the same type, *viz.*, di*iso*propenyl, divinyl, and piperylene and our former conclusions are confirmed and extended.

<div align="center">E X P E R I M E N T A L.</div>

<div align="center">(A) Diisopropenyl.</div>

A solution of pinacol (1 mol.) in acetic anhydride (4 mols.) was introduced drop by drop into warm acetic anhydride in which a small quantity of crystalline phosphoric acid was dissolved. Distillation gave a mixture of di*iso*propenyl and acetic acid, and redistillation over metallic sodium gave di*iso*propenyl, b. p. 69°, $d_4^{20°}$ 0·7262, $d_4^{0°}$ 0·7444 (yield, 85—90%).

The hydrogenation of di*iso*propenyl proceeds at a similar rate to that of isoprene, and the corresponding curve (Fig. 1; 1) is nearly the same, 68—70% of the hydrogen necessary for saturation being absorbed at a uniform velocity. The end of this stage is what we have called " the critical point of hydrogenation of the conjugated system " (*loc. cit.*), for it corresponds to the disappearance of this system. In the next stage the rate of absorption increases, and then falls abruptly to the third and last section. The proportions of hydrogen absorbed in the different sections * as calculated from Fig. 1 are :

Section	1	2	3
Hydrogen, %	69	22·5	8·5

The formula of di*iso*propenyl, $CH_2:CMe\cdot CMe:CH_2$, indicates the following possibilities for the process of hydrogenation : (1) 1 : 2- or 3 : 4-Addition of 1 mol. to give *as.*-methyl*iso*propylethylene. (2) 1 : 4-Addition of 1 mol. to give tetramethylethylene. (3) Addition of 2 mols. of hydrogen, giving di*iso*propyl. It will be shown later that the second section of the curve corresponds to the hydrogenation of methyl*iso*propylethylene, and the third to that of tetramethylethylene. Before the critical point (68—70% of hydrogen absorbed) all three possible substances are formed simultaneously.

The Hydrogenation Process prior to the Critical Point.—In order to study the process of hydrogenation up to the critical point, we interrupted it after the addition of 25% and 50% of hydrogen, and investigated the products. Di*iso*propenyl was removed as a solid compound with sulphur dioxide as in the case of isoprene (*loc. cit.*),

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* The sections of the curves are separated by dashes which are placed on the indefinite intermediate parts of the curve in such a position that these parts are divided in proportion to the velocities of hydrogenation on the horizontal portions concerned.

and the remaining products were estimated by our method of hydrogenation of mixtures.

25% *Hydrogenation.*   To 17·4114 g. of di*iso*propenyl, 2527 c.c. of hydrogen were added (see Table IV, No. 2), and the product was treated with sulphur dioxide at 0° and kept for 8 days.   The liquid was distilled on a steam-bath into a vessel containing alkali at 0°, and the hydrocarbon layer, when separated and distilled over

Time (in minutes).
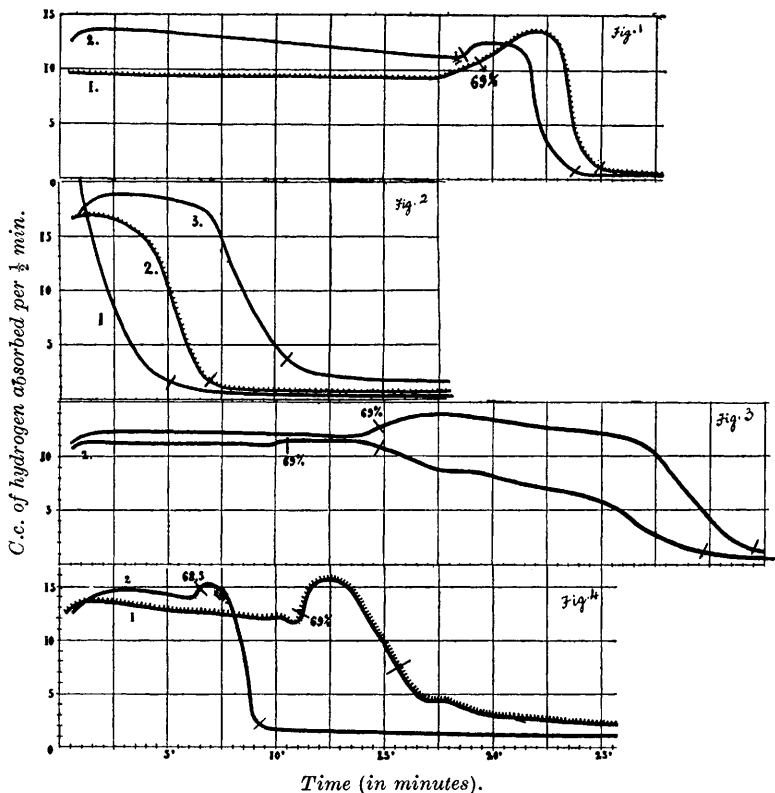
metallic sodium, boiled at 58—68°.   The distillate was then analysed by the hydrogenation method.   For this purpose 2·2385 g. were fully hydrogenated and absorbed 361 c.c.; if the hydrocarbons consisted of hexylenes only, 627 c.c. would have been required; hence the composition was : hexylenes 57·6%; di*iso*propyl 42·4% (see Table IV, No. 4).   From the hydrogenation curve (Fig. 2; 1) we can determine the composition of the hexylenes.   The first section (up to the dash) pertains, as will be shown later, to methyl-*iso*propylethylene, and the second to tetramethylethylene.   In

Table I are given the amounts of hydrogen absorbed in different sections of the curve and the calculated compositions of the reduction products; Table II shows the composition of the original product of hydrogenation.*

TABLE I.

	25% Hydrogenation.		50% Hydrogenation.	
	C.c. of H_2 absorbed.	Components, %.	C.c. of H_2 absorbed.	Components, %.
as.-Methylisopropylethylene	98	15·5 }57·5	173	38 }61
Tetramethylethylene	263	42	105	23
Diisopropyl	0	42·5	0	39
Total	361	100	278·5	100

TABLE II.

Degree of hydrogenation.	25%.		50%.		69%. Exptl. data upon which diagram was based.
	Exptl. data.	Data † from diagram.	Exptl. data.	Data † from diagram.	
Diisopropenyl	64·9%	64%	28%	28%	0%
Diisopropyl	14·9	14	28	28	38
as.-Methylisopropyl-ethylene	5·4 }20·2	16 }22	27·4 }44	32 }44	45 }62
Tetramethylethylene ...	14·8	6	16·6	12	17
Total 100		100	100	100	100

† See p. 2195.

50% Hydrogenation. To 14·228 g. of diisopropenyl, 4187 c.c. of hydrogen (1 mol.) were added. The hydrogenation product was freed from diisopropenyl as before, and kept saturated with sulphur dioxide for 10 days. When freed from the residue and distilled over metallic sodium, the hydrocarbons boiled at 57—68°. The composition of this mixture was investigated by the hydrogenation method : 1·5969 g. of substance absorbed 278·5 c.c. of hydrogen; if the hydrocarbons consisted of hexylenes only, 456·5 c.c. would have been required. The composition was therefore hexylenes 61%, diisopropyl 39% (see Table IV, No. 5).

The nature of hexylenes as determined by the examination of the two sections of the curve (Fig. 2; 2) leads to the results given in Table I, from which it is possible to deduce the composition of the product before its treatment with sulphur dioxide, having regard to the fact that at 50% hydrogenation the amount of diisopropyl

* The calculation is as follows : 100 Mols. of diisopropenyl require 50 mols. of hydrogen for 25% hydrogenation; if x mols. of hexylenes and y of diisopropyl have been formed, we have $x + 2y = 50$, and $x : y = 57·5 : 42·5$; hence $x = 20·2$; $y = 14·9$; and diisopropenyl (by diff.) = 64·9.

formed is equal to the quantity of di*iso*propenyl remaining in the mixture. The composition thus calculated is shown in Table II.

In order to decide which section of the curve relates to *as.*-methyl-*iso*propylethylene, the product * of 50% hydrogenation (freed from di*iso*propenyl) was hydrogenated in admixture with a standard asymmetrically disubstituted ethylene, *viz.*, camphene ; in Table III are shown (1) the amounts of hydrogen required in the various stages as calculated from the weight taken ; (2) the amount of hydrogen actually absorbed by the hydrogenation (for numerical data, see Table IV, Expt. 6). Fig. 2, No. 3 is the corresponding curve. The table and the curve clearly show that camphene is hydrogenated in the first section of the curve ; hence, according to the rule given in Part I (J., 1925, **127**, 417), *as.*-methyl*iso*propylethylene is also hydrogenated in this section and tetramethylethylene in the second.

TABLE III.

C.c. of hydrogen absorbed in the sections of the hydrogenation curve for the mixture with camphene.

	Calc.	Found.
Section 1	108 + 201	312
Section 2	702	690
Total	810 + 201	1002
	1011	

69% *Hydrogenation* (*up to the critical point*). In Part II (*loc. cit.*) two methods of determining the critical point were described. (1) It corresponds to a break in the curve at the end of the first stage, such as is clearly seen at 69% hydrogenation in Figs. 1 and 4. (2) It can be deduced from the amount of di*iso*propenyl present at any moment of the process before the critical point, for the line representing this amount (see Fig. 5) cuts the axis of abscissæ at the percentage of hydrogenation corresponding to the critical point. In the product of 50% hydrogenation the amount of di*iso*propenyl was 28% (see Table II), and the continuation of the line through this point cuts the axis at 69·5%, in agreement with the value obtained by method (1).

As the conjugated system is no longer present beyond the critical point, the treatment of the product by sulphur dioxide becomes unnecessary, and the risk of isomerising the unsaturated substances (see Part II) is avoided. For the addition of the remaining 31% of hydrogen we have two well-defined sections of the curve : the first,
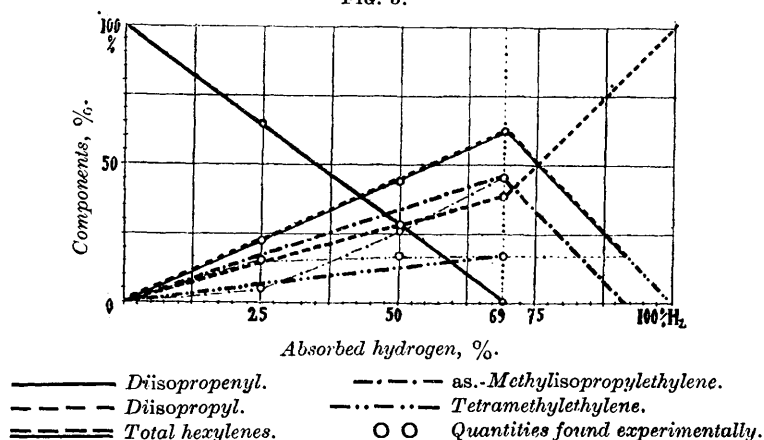
* The composition of the product used in this experiment differed from that mentioned in Table I. It was : saturated substance, 33 ; methyl*iso*propylethylene, 9 ; tetramethylethylene, 58%.

pertaining to methyl*iso*propylethylene, corresponds to 22·5% of hydrogen, and the second, relating to tetramethylethylene, to 8·5% (see p. 2191). The amounts of hexylenes corresponding to different sections are obtained by doubling the percentage of hydrogen absorbed over these sections. The composition calculated in this way is given in the third part of Table II.

General Survey of the Hydrogenation of Di*iso*propenyl.

The diagram representing the hydrogenation of di*iso*propenyl (Fig. 5) is based on the data given in Table II. It is similar to that of isoprene, as might be anticipated from the similarity of the two critical points, *viz.*, 68—70% for di*iso*propenyl and 69—71% for

FIG. 5.

Absorbed hydrogen, %.

——————— Di*iso*propenyl.	—·—·— as.-*Methyliso*propylethylene.
— — — — Di*iso*propyl.	—··—··— *Tetramethylethylene.*
======= *Total hexylenes.*	O O *Quantities found experimentally.*

isoprene. A further resemblance is to be found in the fact that the experimentally determined quantities of di*iso*propenyl, di*iso*propyl, and *total* hexylenes lie on practically straight lines.

The lines for individual hexylenes, however, show breaks, doubtless owing to the circumstance that the relative quantities at 25% and 50% hydrogenation are altered by isomerisation during the treatment with sulphur dioxide, which, as shown later, rapidly converts *as.*-methyl*iso*propylethylene into tetramethylethylene. It is therefore improbable that the deviations are real; on the contrary, there is reason to believe that the curves should be straight lines, as shown by the thicker lines in the diagram. In Table II there are two sets of figures each for 25% and 50% hydrogenation; the experimental values are affected by the isomerisation, whereas the others were obtained from the diagram and are more likely to be correct.

Hydrogenation of Diïsopropenyl mixed with Standard Ethylenic Derivatives of Different Degrees of Substitution.

We undertook the hydrogenation of mixtures of di*iso*propenyl with ethylenic derivatives in order (1) to obtain sufficient hydrogenation curves to determine the position of the critical point, and (2) to determine the course of formation of the saturated molecules in the hydrogenation of a conjugated system. The numerical data and the results obtained are summarised in Tables IV, V, and VI. In Tables V and VI are shown (1) the amounts of hydrogen calculated for the three sections of the curve of di*iso*propenyl according to the scheme on p. 2191, and (2) the amounts of hydrogen which are actually absorbed in the sections of the curve in the hydrogenation of di*iso*propenyl in admixture with the standard ethylenic derivatives.

From Tables IV, V, and VI and the corresponding curves we note the following circumstances. The added standard ethylenic derivatives are generally hydrogenated after the critical point in the places determined by their degree of substitution. Thus, camphene is hydrogenated in the second section of the curve (Fig. 3; 1), together with methyl*iso*propylethylene, and tetramethylethylene in the third section (Fig. 4; 2). Crotonic acid (Fig. 3; 2) and trimethylethylene * (Fig. 4; 1), having no other substance of the same degree of substitution among the hydrogenation products, form a new section inserted between sections 2 and 3. Yet the *iso*propylethylene, added as a standard monosubstituted ethylene, is hydrogenated in the first section together with the conjugated system (Fig. 1; 2). The critical point retains its position and is clearly defined in every case.

The Formation of Fully Saturated Molecules prior to the Critical Point.—The hydrogenation in admixture with camphene requires a special study. Here two facts are of importance : (1) The beginning of the hydrogenation of an *as.*-disubstituted ethylene either formed in the actual process (methyl*iso*propylethylene) or added initially (camphene; methyl-*tert.*-butylethylene †), is distinctly separated from the end of the first section. (2) The whole of the *as.*-disubstituted standard added is hydrogenated after the

* In the case of this compound, the volume of hydrogen in the second section is increased at the expense of the third section (compare Table IV, No. 10 and Table VI). This occurred because the trimethylethylene used contained some *as.*-methylethylethylene which, being an *as.*-disubstituted ethylene, is naturally hydrogenated together with the similarly substituted methyl*iso*propylethylene. The curve is very long and only a part of the third section is included.

† The hydrogenation of di*iso*propenyl in admixture with *as.*-methyl-*tert.*-butylethylene has given the same results as with camphene.

TABLE IV.

*Numerical data for di*isopropenyl *hydrogenated totally, partially, and in admixture with monosubstituted derivatives.*

[0·2 g. of Pt was used throughout except in Expts. No. 1 (0·3 g.) and No. 7 (0·25 g.).]

Expt. No.	Material.	Weight (g.).	C.c. of H₂ calc.	obs.	Temp.	Press. (mm.).	Alcohol (c.c.).	Bath temp.	Curve No.
1	$C_6H_{10} + 2H_2$	0·8884	507	507	13°	758	35	0°	Fig. 1 (1)
2	$C_6H_{10} + \frac{1}{2}H_2$	17·4114	2527	2527	20	760	70	16·5	
3	$C_6H_{10} + H_2$	14·228	4187	4187	19	755	30	16	
4	$C_6H_{10} + \frac{1}{2}H_2$ freed from C_6H_{10}	2·2385	627	361	18	770	35	14·25	,, 2 (1)
5	$C_6H_{10} + H_2$ freed from C_6H_{10}	1·5969	456·5	278·5	16	750	35	14	,, 2 (2)
6	{ $C_6H_{10} + H_2$, freed { from C_6H_{10}, + { camphene	4·194 1·1574	810 } 201 } 1002		12	750	15	14	,, 2 (3)
7	{ Di*iso*propenyl + { *iso*propylethylene	0·6067 0·7438	332 } 252 } 580·5		19	765	30	17	,, 1 (2)
8	{ Di*iso*propenyl + { camphene	0·8840 1·5288	505 } 264 } 760		14	760	15	14	,, 3 (1)
9	{ Di*iso*propenyl + { crotonic acid	0·6100 0·8000	350 } 218·5 } 559		20	775	40	16	,, 3 (2)
10	{ Di*iso*propenyl + { trimethylethylene	0·6930 0·4910	403 } 165·5 } 555		21	770	30	17·5	,, 4 (1)
11	{ Di*iso*propenyl + { tetramethyl- { ethylene	0·4641 0·3597	263 } 100 } 357		17	770	15	14	,, 4 (2)

TABLE V.

*C.c. of hydrogen absorbed in the sections of the di*isopropenyl *curve when hydrogenated in admixture with :*

Section.	*iso*Propyl- ethylene. Calc.	Found.	Camphene. Calc.	Found.	Tetramethyl- ethylene. Calc.	Found.
1. Conjugated system	229+252	475	350	360	180	178
2. Methyl*iso*propyl- ethylene	75	80	110+264	358	58	59
3. Tetramethyl- ethylene	28	25	45	42	25+100	120
Total	332+252	580	505+264	760	263+100	357
	584		769		363	

TABLE VI.

*C.c. of hydrogen absorbed in the sections of the di*isopropenyl *curve when hydrogenated in admixture with :*

	Crotonic acid. Calc.	Found.	Trimethyl- ethylene. Calc.	Found.
Section 1. Conjugated system	242	230	278	277
,, 2. Methyl*iso*propylethylene	77	85	91	105·5
Section of the components added	—	213	—	135·5
,, 3. Tetramethylethylene	31	31	34	37
Total	350	559	403	555

critical point, and therefore does not alter the amount of fully saturated molecules formed before this point. This suggests that the fully saturated molecules formed before the critical point are not formed directly from the component to which the section relates, but from the conjugated system by addition of 2 mols. of hydrogen, either simultaneously or in such a rapid succession as to appear to be so.

Hence, of the two assumptions made in Part II (this vol., p. 834), the second is obviously correct.

Isomerisation of as.-Methyl*iso*propylethylene by the Action of Sulphur Dioxide.

We stated above (p. 2194) that the use of sulphur dioxide caused an isomerisation which affected the apparent composition of the hydrogenation products of di*iso*propenyl. In order to demonstrate this, the 50%-hydrogenation product, freed from di*iso*propenyl, was saturated with sulphur dioxide at 0°, and kept in a sealed tube at 100° for 3 days. The resulting hydrocarbons were freed from sulphur dioxide and analysed by the hydrogenation method : 2·049 g. absorbed 352 c.c., whereas 577 c.c. of hydrogen would have been required if the hydrocarbons contained hexylenes only ; hence the composition was : hexylenes 61%, di*iso*propyl 39%. The hydrogenation curve has two sections : in that corresponding to methyl*iso*propylethylene 44 c.c. were absorbed, equivalent to 7·5% of this hydrocarbon, and the absorption of 308 c.c. in the other section indicated 53·5% of tetramethylethylene.

Comparison of these proportions with those for the original material (Table I) shows a large decrease (38 to 7·5%) for methyl-*iso*propylethylene and a corresponding increase (23 to 53·5%) in tetramethylethylene. Moreover, these changes are much more extensive than those involving the amylenes derived from isoprene (see Part II, p. 835).

(B) Divinyl.

Divinyl, prepared by pyrogenetic decomposition of naphtha, was converted to the tetrabromide (m. p. after recrystallisation 113—115°), regenerated by zinc in alcoholic solution, and collected over saturated brine. A measured volume (usually 200—300 c.c.) was dissolved in alcohol containing platinum-black and hydrogenated at 0°, the amount of divinyl taken being calculated from the volume of hydrogen absorbed. The hydrogenation curve is given in Fig. 7.
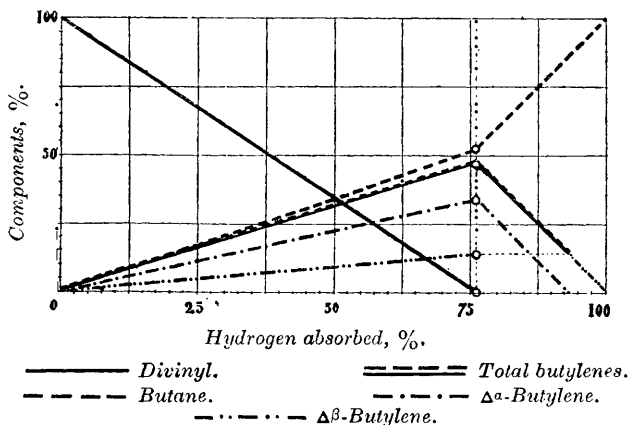
In the hydrogenation of divinyl, $CH_2\text{:}CH\cdot CH\text{:}CH_2$, three products can be formed, viz., $n\text{-}\Delta^\alpha$- and Δ^β-butylene and butane. The rules given in Part I (loc. cit.) postulate three sections on the curve, and these can, in fact, be observed. The first, relating to the conjugated

system, ends at the critical point; the second pertains to Δ^α-, and the third to Δ^β-butylene. The presence of the $1:4$ hydrogenation product proves that divinyl belongs to our Type II of conjugated systems. The critical point on the curve is at 76% of hydrogenation. The amounts of hydrogen absorbed in the different sections as calculated from Fig. 7 are :

Section	1	2	3
Hydrogen, %	76	17	7

Calculation from the hydrogen absorbed in the sections of the curves for divinyl in admixture with trimethylethylene (Fig. 8; 3) and with tetramethylethylene (Fig. 9; 2) gives similar figures. These two offer a good example for such a calculation, for on both curves all

Fig. 6.

Hydrogen absorbed, %.

———————— Divinyl. ═ ═ ═ ═ Total butylenes.
— — — — Butane. — ·— ·— Δ^α-Butylene.
— ··— ··— Δ^β-Butylene.

the divinyl is hydrogenated before the admixed substances. The figure 100% on these curves shows the point where the hydrogenation of divinyl is completed. The first of these curves shows clearly all the three sections; on the second the limits of the third section are very clearly marked. The composition of the hydrogenation product at the critical point, as calculated from the amounts of hydrogen absorbed, is : Divinyl, 0; butane, 52; Δ^α-butylene, 34; Δ^β-butylene, 14%; and Fig. 6 is constructed from these values.

Hydrogenation of Divinyl in Admixture with Monoethylenic Derivatives of Different Degrees of Substitution.—The curves in Figs. 7, 8, and 9 represent the hydrogenation of divinyl in admixture with ethylenic derivatives, and, in conjunction with the data of Tables VII and VIII, they provide the material necessary for following the course of the process. Both for divinyl alone and for its mixtures

the critical point is at 76% of hydrogenation. As in the case of other conjugated systems of Type II, the position of the critical point is not always clearly marked. The curve for the mixture with Δ^β-butylene (Fig. 8; 2) is very similar to that of pure divinyl (Fig. 7), but is more prolonged in the last section. The dash marked 100% on the curves indicates the point where, by calculation, divinyl is consumed and hydrogenation of the admixed component begins.

Time (in minutes).
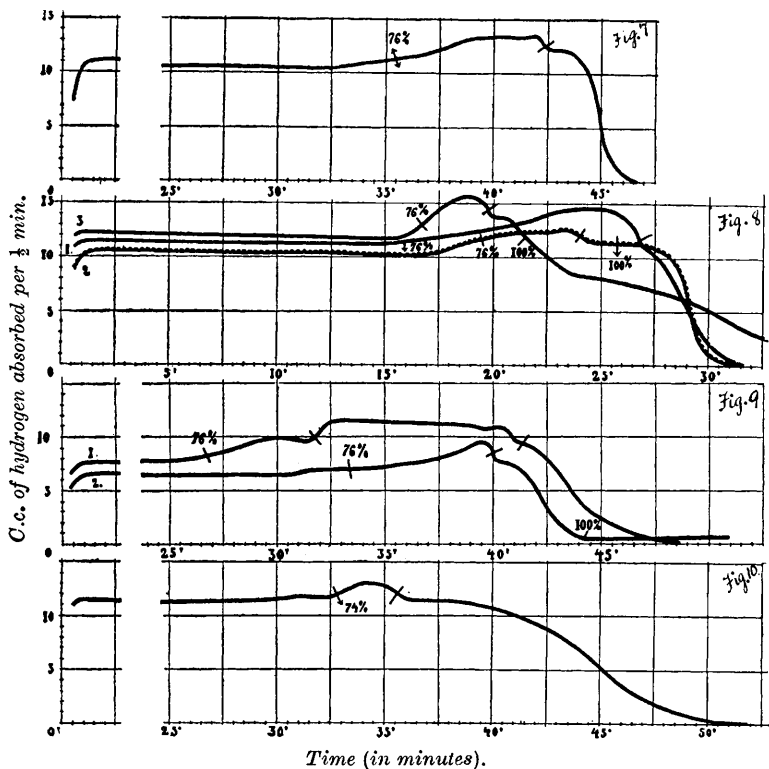
(C) *Piperylene.*

Piperylene, $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH_3$, was obtained from piperidine by Hofmann's method (*Ber.*, 1881, **14**, 664); it had b. p. 41·5°; $d_4^{20°}$ 0·6852. In spite of its unsymmetrical nature, piperylene can yield only two pentenes on hydrogenation, for the 1 : 2 and 1 : 4 addition of 1 mol. of hydrogen both lead to the same *s.*-methylethylethylene. It is therefore impossible to determine whether 1 : 4-addition actually occurs, but the properties of piperylene (*e.g.*, its tendency to polymerise, and its energetic

TABLE VII.

Numerical data for divinyl hydrogenated alone and in admixture with monoethylenic derivatives.

(Bath temperature, 0°; weight of Pt, 0·2 g.; vol. of alcohol, 50 c.c.)

Expt. No.	Material.	Vol. (c.c.).	Weight (g.).	C.c. of H_2 calc.	C.c. of H_2 obs.	Temp.	Press. (mm.).	Curve No.
1	Divinyl	490		980	980	17°	765	Fig. 7
2	{ Divinyl + { *iso*propylethylene	223	0·7606	446 } 257 } 705	17	760	,, 8 (1)
3	{ Divinyl + { Δ$^\beta$-butylene	266 80		532 } 80 } 600	18	760	,, 8 (2)
4	{ Divinyl + { camphene	266	1·2098	532 } 211 } 734	19	765	,, 9 (1)
5	{ Divinyl + { trimethylethylene	264	0·5138	528 } 173 } 697	18	765	,, 8 (3)
6	{ Divinyl + { tetramethylethylene	287	0·210	574 } 59 } 629	18	760	,, 9 (2)

TABLE VIII.

C.c. of hydrogen absorbed in the sections of the curve when divinyl is hydrogenated in admixture with :

Section.	*iso*Propyl-ethylene. Calc.	*iso*Propyl-ethylene. Found.	Δ$^\beta$-Butylene. Calc.	Δ$^\beta$-Butylene. Found.	Camphene. Calc.	Camphene. Found.	Trimethyl-ethylene. Calc.	Trimethyl-ethylene. Found.	Tetramethyl-ethylene. Calc.	Tetramethyl-ethylene. Found.
1	339	377	405·5	390	419	403	416·5	397	435·5	436
2	76 + 257	289	81	90·5	97	89	93·5	88	97·5	100
A *	—	—	—	—	211	216	—	—	—	—
3	31	39	37·5 + 80	120·5	39	54	38	42	40	40
B *	—	—	—	—	—	—	173	170	59	53
Total	446 + 257	705	524 + 80	601	763	762	721	697	632	629
	703		604							

* The sections thus denoted are due to substances which, in the absence of similarly substituted compounds among the products of hydrogenation, have formed their own sections.

reaction with sulphur dioxide) would suggest that some of the *s.*-methylethylethylene is formed in this way.

Piperylene evidently belongs to our Type II of conjugated systems. Its hydrogenation curve (Fig. 10) has three sections : that before the critical point (74% hydrogenation) is nearly horizontal; the second, due to propylethylene, corresponds to the more rapid absorption of 6·5% of hydrogen; and the third (19·5% of hydrogen) relates to *s.*-methylethylethylene (see Table X).

The amounts of hydrogen absorbed in the corresponding sections of the hydrogenation curves of piperylene in admixture with different derivatives of ethylene give nearly similar figures, the critical point usually corresponding to 72% hydrogenation (see Table IX).

The figures of the last column serve to calculate the composition of the hydrogenation product at the critical point. The amount of the particular pentene corresponding to each section is obtained by doubling the percentage of hydrogen absorbed over that section;

TABLE IX.

Percentages of hydrogen absorbed in the sections of the curves for piperylene.

No. of Fig. and curve	10.	12 (1).	12 (2).	12 (3).	13 (2).	Mean.
Section 1	74	73—75	72	72	72	73
,, 2	6·5	9—7	8	8	8	7·5
,, 3	19·5	18	20	20	20	19·5

the amount of pentane is obtained by difference. The composition thus calculated is : Piperylene, 0; propylethylene, 15; *s.*-methylethylethylene, 39; pentane, 46%. From these values in conjunction with Table IX, Fig. 11 is plotted by the method used in the case of di*iso*propenyl (Fig. 5).
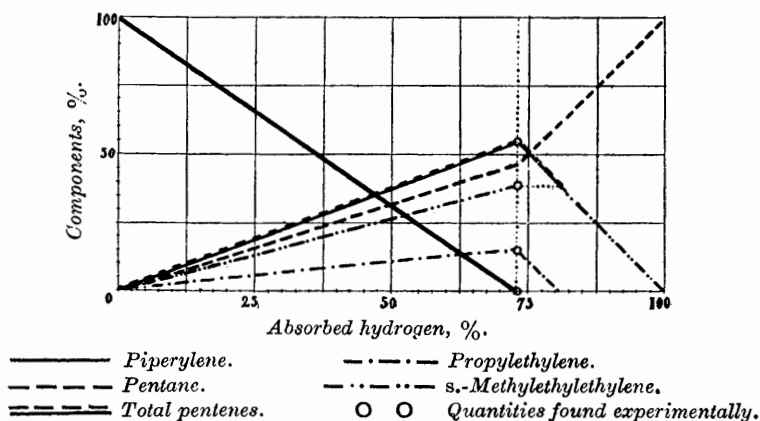
FIG. 11.

Absorbed hydrogen, %.

——————— *Piperylene.*   — · — · — *Propylethylene.*
— — — — *Pentane.*   — ·· — ·· — *s.-Methylethylethylene.*
════════ *Total pentenes.*   O O   *Quantities found experimentally.*

TABLE X.

Numerical data for piperylene hydrogenated alone and in admixture with monoethylenic derivatives.

(0·2 G. of Pt and 15 c.c. of alcohol were used in each experiment except the first, for which 0·25 g. and 25 c.c., respectively, were used.)

Expt. No.	Material.	Weight (g.).	C.c. of H_2 calc.	obs.	Temp.	Press. (mm.).	Bath temp.	Curve No.
1	Piperylene	1·4539	1022	1015	14°	750	12·75°	Fig. 10
2 {	Piperylene	0·4515	316 }	504	15	757	13·75	,, 12 (1)
	Safrole	1·3050	192 }					
3 {	Piperylene	0·4819	331·5 }	491	15	767	14·25	,, 12 (2)
	Camphene	1·0038	172 }					
4 {	Piperylene	0·4287	304 }	760	16	745	13·5	,, 12 (3)*
	Anethole	2·9340	480 }					
5 {	Piperylene	0·4940	344 }	542	13	755	10·5	,, 13 (1)*
	Methylheptenone	1·1224	210 }					
6 {	Piperylene	0·5881	409 }	484·5	16	758	13·5	,, 13 (2)*
	Tetramethylethylene	0·2697	76 }					

* A dash marked 100% on these curves indicates the point where piperylene is consumed and the hydrogenation of the admixed substance begins.

Hydrogenation of Piperylene Mixed with Standard Ethylenic Derivatives of Different Degrees of Substitution.—We have examined a number of mixtures of piperylene with ethylenic derivatives of different degrees of substitution. The numerical data for these mixtures are in Tables X and XI. The construction of Table XI is similar to that of Table V.
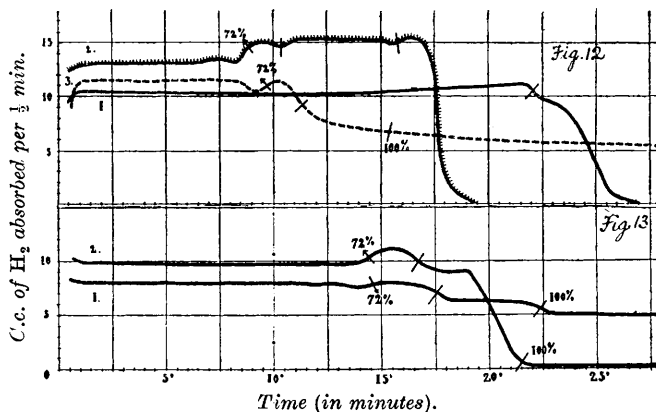

Time (in minutes).

TABLE XI.

Section	Safrole.		Camphene.		Anethole.		Methyl-heptenone.		Tetramethyl-ethylene.	
	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.
1 } 2 }	255+192	454	242 25	235 27	222 23	213 22	251 26	240 30	299 31	292 32
A	—	—	172	164	—	—	—	—	—	—
3	61	30	64	65	59+480	530	67	70	79	86
B	—	—	—	—	—	—	210	202	76	74
Total	316+192	504	332+172	491	304+480	765	344+210	542	409+76	484
	508		504		784		554		485	

From Tables X and XI the following facts emerge. (1) In the mixture of piperylene with safrole (a monosubstituted ethylene) the critical point is not clearly marked, for the safrole is partially hydrogenated in the first section (Fig. 12; 1). (2) The mixture with camphene gives a peculiar curve, for this *as.*-disubstituted ethylene has no pentene of the same degree of substitution among the products of hydrogenation; hence it forms an independent section (A) on the curve. (3) Anethole (Fig. 12; 3) and *s.*-methylethylethylene, being of the same degree of substitution, hydrogenate simultaneously. (4) Methylheptenone (Fig. 13; 1) and tetramethylethylene (Fig. 13; 2), like camphene, form independent sections (B). These derivatives of ethylene are to be found in the last sections of the curves in the places determined by their degree of substitution.

Summary.

(1) The study of the hydrogenation of di*iso*propenyl confirms and extends the general conclusions previously drawn from the study of isoprene.

(2) The amounts of all the components formed during the process of hydrogenation are shown in the hydrogenation diagram of Type II of conjugated systems as straight lines joining the zero point of the diagram with the corresponding points lying on the ordinate of the " critical point of hydrogenation."

(3) Saturated compounds are formed before the critical point is reached, because some molecules add two molecules of hydrogen simultaneously.

(4) The mono-ethylenic derivatives of different degrees of substitution, either formed in the process of hydrogenation or added initially, are hydrogenated after the critical point in places determined by their degrees of substitution. The mono-substituted ethylenes do not follow this rule, but hydrogenate partially or completely before the critical point.

(5) Piperylene and divinyl belong to Type II of conjugated systems. Diagrams are constructed showing the whole course of hydrogenation of these hydrocarbons.

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