# **374.** *Liquid-phase Reactions at High Pressures. Part II. The Polymerisation of Olefins.*

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The polymerisation of the following substances has been studied at temperatures of 100—160° and pressures up to 10,000 atmospheres: α-methylstyrene, αβ-dimethylstyrene, α-*iso*propenylnaphthalene, *as*-diphenylethylene, ethyl cinnamate, *iso*amylene, and $\Delta^{\gamma}$-butenylbenzene.

α-Methylstyrene, which is polymerised only to a low degree and with difficulty by the usual methods, is readily converted at 100° and 5000 atmospheres into a glassy polymer, containing about 50 molecular units. Lower polymers, resembling those formed in the presence of catalysts, are obtained by pressure polymerisation at higher temperatures. The formation of the lower polymers follows a different course from the high polymerisation, and high polymers cannot be made by the application of high pressure to the unsaturated dimer of α-methylstyrene.

High polymerisation among the substances studied is only realised in compounds of the type Aryl·CR:$CH_2$.

WHEN organic molecules polymerise they normally do so to yield substances of greater stability (at reasonably low temperatures) and lower molecular volume. Hence the reaction is one which would be expected to be favoured by increase in pressure.

Conant and Tongberg (*J. Amer. Chem. Soc.*, 1930, **52**, 1659) observed the ready polymerisation of isoprene under 12,000 atm. pressure at room temperature, and Tammann and Pape (*Z. anorg. Chem.*, 1931, **200**, 113) noted that pressures up to 3000 atm. had a greater influence on the polymerisation of olefins than on the other liquid-phase reactions studied by them. A particular advantage of high pressure as a means of effecting polymerisation is that it may bring about reaction under comparatively mild conditions, and thereby diminish disturbing influences of high temperatures and drastic catalysts.

The present paper deals with explorative work on the polymerisation of some substituted ethylenes, and particularly of α-methylstyrene, at pressures up to 10,000 atm., and at temperatures of 100—*ca.* 160°.

It is well known that styrene itself readily polymerises, under various conditions of temperature and catalyst, the degree of polymerisation being 10—1000-fold (Staudinger *et al.*, *Ber.*, 1929, **62**, 241, 2912, 2921). In general agreement with Tammann and Pape (*loc. cit.*), we find that at 100°, under 5000 atm. pressure, styrene is polymerised to a tough, colourless glass. This is slowly dissolved by cold benzene, and precipitated in a fibrous form when the solution is slowly dropped into cold methyl alcohol.

α-Methylstyrene, on the other hand, is not easily polymerised to material of high molecular weight by the usual low-pressure methods. For instance, Staudinger and Breusch (*Ber.*, 1929, **62**, 442) found that the trimer was the highest polymer produced by heating alone, or by the action of Florida earth or boron trichloride. Ultra-violet light gave only a dark gum and unchanged monomer, and stannic chloride gave 4—5% of octamer, the main product being the saturated dimer.

By employing a pressure of 5000 atm. at 100°, we have obtained 85% of a mixture of high polymers with a mean molecular weight of about 5600, corresponding to an aggregation of about 50 molecules, the remaining 15% being substantially all monomer. The results of a similar series of experiments at pressures of 2000—10,000 atm. and temperatures of 100—*ca.* 160° are given in Table I.

TABLE I.

*Effect of Temperature and Pressure on the Molecular Weight and Yield of Polymers from α-Methylstyrene.*

| Temp. | Press., atm. | Time, hrs. | Yields, %. Monomer. | Yields, %. Low polymers. | Yields, %. High polymers. | Mean mol. wt. of high polymers. |
|---|---|---|---|---|---|---|
| 100° | 5,000 | 1 | 98—99 | — | — | 5,400—5,800 |
| | | 14 | 32·6 | 3·4 | 64·0 | |
| | | 96 | — | — | 85 | |
| 110 | 3,500 | 95 | 23 | 12 | 65 | 2,600 |
| 120 | 2,000 | 96 | 68·3 | 27·2 | 4·5 | 1,600 |
| | | 260 | 46·0 | 48·7 | 5·3 | |
| 125 * | 4,000 | 96 | 48·6 | 43·0 | 8·4 | 1,500 |
| 125 | 4,000 | 96 | 46·4 | 27·7 | 26·0 | 1,050 |
| | 10,000 | 47 | 21·0 | | 79·0 | 1,170 |
| 150 | 4,000 | 48 | 18·1 | 81·9<br>($M = 370$) | None | — |

* 50% dilution with pure benzene.

The main points which arise are as follows: (1) Polymerisation of α-methylstyrene was induced by pressures of the order of 2000 atm. upwards at temperatures of about 100° without the aid of added catalysts. (2) Such agents as were used (dry hydrogen

TABLE II.

*α-Methylstyrene.*

*Effect of catalysts on the yields and molecular weights of polymers.*

Temp. = 120—125°; press. = 4000 atm.

| Time, hrs. | Catalyst (0·25% by wt.). | Yield, %, of Monomer. | Low polymers. | High polymers. | Mean *M* of highest polymers obtained. |
|---|---|---|---|---|---|
| 96 | None | 46·4 | 27·7 | 26·0 | 1050—970 |
| 96 | Dry HCl | 21·5 | 51·9 | 26·6 | 860—940 |
| 96 | Dry HCl | 16·5 | 57·5 | 26·0 | 860—940 |
| 48 | Benzoyl peroxide | 55·0 | 26·0 | 19·0 | 1000—1070 |
| 96 | $ZnCl_2$ (anhyd.) | 9·5 | 90·5 | None | 370—380 |

chloride, benzoyl peroxide, anhydrous zinc chloride) did not appear to accelerate the reaction or lead to the production of polymers of higher molecular weight than those produced without a catalyst under the same conditions of temperature and pressure. The main effect of these added materials appeared to be to increase the yield of lower polymers at the expense of the monomer (see Table II). Zinc chloride prevented the production of any high polymer. (3) Although an increase of pressure at a given temperature did not materially affect the mean molecular weight of the higher polymers, yet it occasioned a considerable increase in the yield; *e.g.*, 26% in 96 hours at 4000 atm. and 79% in 47 hours at 10,000 atm., both experiments at 125°. (4) The effect of increased temperature was very marked, there being a decided fall in the molecular weight of the high polymers as the temperature was increased from 100° to 150°. This effect of an increase in temperature on the degree of polymerisation is well known; *e.g.*, Staudinger, Ashdown, Brunner, Bruson, and Wehrli (*Helv. Chim. Acta*, 1929, **12**, 936) recorded a decrease in the molecular weight of the polymers of indene from 3500 to 1500 when the temperature of polymerisation with stannic chloride was increased from —80° to + 110°.

The high polymers [insoluble in cold benzene–methyl alcohol (1 : 1·5), and in boiling methyl and ethyl alcohols] produced at 100° were precipitated in a fibrous form when a cold benzene solution was dropped into cold methyl alcohol. Those from experiments at 110° or higher, on the other hand, were precipitated in a powdery form under like conditions. Whereas experiments at 100° gave polymers with a molecular weight of about 5600, those produced at 110° had a molecular weight of about 2600. The molecular weight further decreased to 1100 at 125°, and to 370 at 150—155°.

The mean molecular weight of the highest polymer obtained indicated that it was still in the class of hemicolloids, on the basis of Staudinger's classification. Nevertheless, the material possessed in some respects the properties of the more complex (eucolloid) type—for example, the glassy nature, the tendency to precipitate in fibres, and some ability to swell on being moistened with solvents.

This material was not fractionated beyond the elimination of heptamer and lower polymers, and it is very probable that it contained some material of higher molecular weight, which might confer some eucolloidal properties.

To find whether the polymers produced at 100° were depolymerised by an increased temperature while the pressure was maintained constant, the following experiment was carried out. A sample of the monomer was subjected to 5000 atm. pressure for 96 hours at 100°, *i.e.*, to conditions under which 85% of polymer with a mean molecular weight of 5600 had been obtained. The temperature was then raised to *ca.* 125° during 6—8 hours, and maintained thereat for a further 78 hours while the pressure was kept constant at 5000 atm. The product yielded 85% of high polymer which was still precipitated in a fibrous form. It was not homogeneous, however, and gave molecular weight figures from 6100 to 3000. Constant values were only obtained after repeated grinding and mixing. Some depolymerisation had obviously taken place.

A further point of interest was that, although at 100° the amount of low polymers present was very small (3·4%), yet at 125° their amount was about the same as that of the high polymers (28% and 26%). The low polymers from experiments at 125° were found to contain dimer, trimer, and possibly tetramer. At 100°, however, practically all the material which had not polymerised to high polymer was recoverable as monomer. It would seem, therefore, that under the experimental conditions two distinct types of polymerisation are possible, and that these take place at temperatures very narrowly separated. At 100° under high pressure α-methylstyrene polymerises probably by a chain mechanism to a high but not to a low polymer. At slightly higher temperatures a stepwise type of reaction becomes prominent, and low polymers can be isolated from the product. At 150° only the stepwise reaction seems to take place, and is itself limited to the production of tetramer as the highest polymer.

These findings fall into line with previous observations at ordinary pressures. Stepwise reactions leading only to low polymers are well known; *e.g.*, it has been shown that distyrene and tristyrene do not form polystyrenes (Staudinger and Steinhofer, *Annalen*, 1935, **517**, 41). Similarly, we have found that the unsaturated dimer of α-methylstyrene does not polymerise when subjected to a pressure of 5000 atm. at 100° for 91 hours. The material was recovered unchanged, and there was no sign of polymerisation or cyclisation to the saturated dimer. This fact provides convincing evidence that the polymerisation can take at least two totally different courses.

The polymerisation of α-methylstyrene by means of stannic chloride yields a large proportion of a saturated dimer, m. p. 52° (Staudinger and Breusch, *loc. cit.*; Tiffeneau, *Ann. Chim.*, 1906, **10**, 155), which has been proved by Bergmann, Taubadel, and Weiss (*Ber.*, 1931, **64**, 1493) to be a derivative of indene. No such material could be isolated from the dimer produced in experiments at 125° without a catalyst, even when the products were seeded with a preparation of the saturated dimer and kept for some months in the dark, with occasional cooling and scratching. They were all unsaturated towards bromine in carbon tetrachloride. It is clear, therefore, that the dimer prepared under high pressure is essentially an open-chain compound, probably identical with that of Klages (*Ber.*, 1902, **35**, 2639), and that the application of pressure is insufficient to close the indene ring in the absence of a catalyst.

*Other Substituted Ethylenes.*—Comparative experiments have also been carried out with αβ-dimethylstyrene, *as*-diphenylethylene, *iso*propenylnaphthalene, ethyl cinnamate, $\Delta^{\gamma}$-butenylbenzene, and *iso*amylene. The results are summarised in Table III.

TABLE III.

*Substituted Ethylenes other than α-Methylstyrene.*

| | | Experimental conditions. | | | Polymers. | | |
|---|---|---|---|---|---|---|---|
| Substance. | Formula. | Press., atm. | Temp. | Time, hrs. | Yield, %. | *M*. | Order of polymer. |
| Unsat. dimer of α-methylstyrene..... | $CPhMe_2{\cdot}CH{:}CMePh$ | 5,000 | 100° | 91 | No polymerisation | | |
| αβ-Dimethylstyrene... | $CPhMe{:}CHMe$ | 5,000 | 120 | 96 | 2·3 | 251 | 2 |
| α-*iso*Propenylnaphthalene | $C_{10}H_7{\cdot}CMe{:}CH_2$ | 5,000 | 125 | 166 | 1·9 | 905 | 5—6 |
| | | 10,000 | 125 | 30 | 54 | 1270 | 8 |
| *as*-Diphenylethylene | $CPh_2{:}CH_2$ | 5,000 | 120 | 68 | 35·5 | 347 | 2 |
| | | 5,000 | 150 | 96 | 35·2 | — | 2 |
| Ethyl cinnamate ...... | $CHPh{:}CH{\cdot}CO_2Et$ | 4,000 | 125 | 240 | 58·5 | — | — |
| *iso*Amylene ........... | $CMe_2{:}CHMe$ | 5,000 | 125 | 96 | No polymerisation | | |
| | | 10,000 | 125 | 24 | No polymerisation | | |
| $\Delta^{\gamma}$-Butenylbenzene... | $CH_2Ph{\cdot}CH_2{\cdot}CH{:}CH_2$ | 5,000 | 125 | 78 | 2·0 | — | — |
| | | 5,000 | 100 | 96 | 1·9 | — | — |

αβ-Dimethylstyrene gave only about 2% of a polymer, with a molecular weight corresponding to *dimer*, after treatment at 5000 atm. and 120° for 96 hours. Under these conditions α-methylstyrene yields 30% of polymers with a mean molecular weight of 1100 (mainly octamer).

*as*-Diphenylethylene likewise yielded only *dimers*, but to a greater extent (36%). This yield was not materially altered by increase of temperature or of period of reaction. The polymers appeared to be a mixture of dimers, and no sharply melting material could be separated; they did not decolorise bromine solution in the cold, and had a melting range of 100—105°. Lebedev (*Ber.*, 1923, **56**, 2349) records an unsaturated dimer which

Bergmann and Weiss have shown to be ββδδ-tetraphenyl-$\Delta^{\gamma}$-butene, m. p. 113° (*Annalen*, 1930, **480**, 49), and Bergmann and Weiss prepared a saturated dimer, m. p. 143°, which they showed to be 1 : 1 : 3-triphenyl-3-methylhydrindene.

α-*iso*Propenylnaphthalene, on the other hand, polymerised to much the same degree as did α-methylstyrene under similar conditions, but the reaction was much slower. At 125° and 5000 atm. in 166 hours there were formed only 2% of high polymer with a molecular weight of about 900. At 10,000 atm., however, 54% of polymers with a molecular weight of 1300 were produced in 30 hours at the same temperature.

Seeligmann (Diss., Karlsruhe, 1906) noted that allyl cinnamate polymerised at 210° but the propyl ester did not. Liebermann and Zsuffa (*Ber.*, 1911, **44**, 841) found that the ethyl ester polymerised most readily, particularly on distillation followed by exposure to ultra-violet light for long periods and subsequent heating at 80—90°. The products were amorphous, white, infusible, sparingly soluble powders. Subsequently, Liebermann and Kardos (*Ber.*, 1913, **46**, 1055) found that polymerisation of allyl cinnamate by heat yielded products easily hydrolysable with alkali; whereas ultra-violet light yielded quite distinct polymers, resistant to hydrolysis under the same conditions.

At a pressure of 4000 atm. and a temperature of 125° we obtained a 58% yield of powdery polymer of ethyl cinnamate. It did not affect polarised light, and was therefore probably amorphous. It melted with decomposition in a sealed tube at about 320°, but sublimed in an open tube. Liebermann and Zsuffa's poly-ethyl cinnamate (*loc. cit.*) depolymerised and distilled at 273°, yielding ethyl cinnamate. The pressure polymer was easily hydrolysed by alcoholic potash, and would therefore appear to have a structure similar to that of the polymer obtained by heating allyl cinnamate.

We have been unable to detect any polymerisation of *iso*amylene (mainly trimethylethylene) at 125° and 5000—10,000 atm.

The effect of substitution upon the tendency to polymerise under high pressure is thus quite normal. The main conclusions which emerge are: (1) An aromatic group has a great positive influence provided that it is directly attached to the unsaturated centre. (2) High polymerisation among the substances studied has only been realised when this condition is satisfied and when a terminal $CH_2{:}C<$ group is present, *i.e.*, amongst compounds of the type Aryl·CR:$CH_2$. The behaviour of *as*-diphenylethylene shows that high polymerisation is not necessarily given by substances of this type under the experimental conditions used.

## EXPERIMENTAL.

The apparatus and experimental procedure were those described in a previous paper (Newitt, Linstead, Sapiro, and Boorman, this vol., p. 876).

*α-Methylstyrene.*—Phenyldimethylcarbinol was made both by Klages' and by Tiffeneau's methods and was dehydrated following Staudinger and Breusch (*loc. cit.*). Small quantities were prepared at a time, since the hydrocarbon undergoes oxidation, even in the dark, on keeping. The purity was controlled by determination of the refractive index just before use.

The pressure product was treated by the following adaptation of Staudinger and Breusch's method. A hard or very viscous product was dissolved in cold benzene (10 c.c. per g., or 20 c.c. per g. in the case of experiments at 100°) and the cold solution was dropped slowly into 1·5 vols. of cold methyl alcohol with vigorous stirring. The precipitate was collected in the cold and washed with alcohol–benzene. It was then boiled twice with methyl alcohol (25 c.c. per g.) and twice with ethyl alcohol (25 c.c. per g.), the mixture being filtered hot each time. The solid product was pressed on a porous tile and dried for several days in a vacuum desiccator. This material, designated " High polymers " in Table I, consisted of a mixture of polymers from which heptamer and lower polymers had been removed.

If the pressure product was fluid it was first fractionally distilled up to *ca.* 200°/14 mm., and the residue was dissolved in benzene and precipitated as above. Monomer and low polymers were recovered from the filtrates and distilled fractions.

The methyl- and ethyl-alcoholic extracts were separately evaporated to dryness, and almost invariably gave negligible quantities of residue, indicating very small proportions of hexamer and heptamer.

Where a catalyst such as hydrogen chloride or zinc chloride had been used, the pressure product in benzene solution was first washed with water, dried over anhydrous sodium sulphate, and then fractionated and precipitated. No precipitate of polymer was obtained from experiments with zinc chloride, and the polymerised material was recovered by evaporation of the solvents.

Molecular weights were determined cryoscopically in " molecular-weight " benzene, a concentration of not more than 3—4% being used. All polymers with a mean molecular weight up to 2600 gave reproducible results, but precipitated polymers containing fibrous material gave less consistent values. The constant for the solvent, determined with several hydrocarbons, and particularly with the saturated dimer of α-methylstyrene (m. p. 52°), was 54·0. Two detailed examples of the determinations are given below, the results as a whole being summarised in Table I.

1. 5000 Atmospheres, 100°, 96 hours.

| | Δ. | *M.* |
|---|---|---|
| 0·3994 G. in 11·70 g. benzene | 0·031° | 5870 |
| 0·4027 G. ,, 11·80 g. ,, | 0·034 | 5430 |

2. 3500 Atmospheres, 110°, 95 hours.

| | Δ. | *M.* |
|---|---|---|
| 0·4855 G. in 14·89 g. ,, | 0·068 | 2600 |
| 0·4839 G. ,, 15·46 g. ,, | 0·065 | 2597 |

[Found, in (2) : C, 91·2, 91·2; H, 8·4, 8·4. Calc. for $(C_9H_{10})_n$ : C, 91·55, H, 8·45%.]

The highest polymer (*M* 5600) was a colourless transparent solid. It could be powdered by hammering, but not by grinding with a pestle and mortar. When the pulverised material was heated in an open tube, the first signs of softening could be detected with a lens at 185° and the first liquid at 222°. The material was completely fluid at 230°. There was no discoloration. When a layer of the powdered material was covered with benzene, the granules became coated with a transparent film, which grew slowly and after 30 minutes was double the width of the original layer. The layer adhered to the tube and persisted after several hours. In chloroform the granules rose, became coated with a gelatinous film, and dissolved fairly quickly to give a viscous solution. In ether the granules rapidly swelled and formed a button. This could easily be broken, by shaking, into particles which did not adhere to the tube. When the high polymer was precipitated from benzene it formed fibres merging into a disc with retained solvent. This hardened after evacuation in a desiccator for some days, and in that form was extremely difficult to pulverise even though very " blistered." It could be easily cut with a knife.

*Low polymers from experiments at* 125°. The low polymers from a number of experiments, weighing 14·3 g. and representing about 27% of the polymerisation yield, were fractionally distilled under 0·1 mm. The fractionation was then repeated. The data are given in Table IV.

TABLE IV.

| Fraction. | B.p./0·1 mm. | Wt., g. | $n_D^{24°}$. | *M.* | Low polymer, %. | | Total polymer, % (approx.). |
|---|---|---|---|---|---|---|---|
| *a* | 110—120° | 2·04 | 1·5765 | 234 | 14·3 | 42·7 | 13·0 |
| *b* | 120—130 | 1·31 | 1·5772 | — | 9·2 | | |
| *c* | 130—175 | 1·40 | 1·5860 | — | 9·8 | | |
| *d* | 175—190 | 1·35 | 1·5923 | 249 | 9·4 | | |
| *e* | 190—210 | 1·13 | 1·60 (approx.) | — | 7·9 | 37·6 | 6·5 |
| *f* | 202—212 | 2·57 | 1·602 ( ,, ) | 315 | 18·0 | | |
| *g* | 212—220 | 1·68 | 1·604 ( ,, ) | 311 | 11·7 | | |
| *h* | > 220 | 0·7 | | — | 4·9 | 8·4 | 2·6 |
| Residue | | 0·5 | | — | 3·5 | | |
| Loss | | 1·62 | | | 11·3 | | |

The dimer fractions (*a*)—(*d*) were seeded with the saturated dimer (prepared by Tiffeneau's method) and kept for some months, being occasionally chilled in ice and salt and rubbed with a glass rod. No crystalline dimer could be isolated. All the fractions instantly decolorised a solution of bromine in carbon tetrachloride.

*Unsaturated Dimer of α-Methylstyrene.*—A sample of unsaturated dimer was prepared by heating phenyldimethylcarbinol to 120° with phosphoric acid (*d* 1·70) (Bergmann, Taubadel, and Weiss, *loc. cit.*). It was distilled four times under 14 mm., after which the first runnings did not give any crystalline saturated dimer on chilling and seeding. The sample had b. p. 172°/14 mm., and $n_D^{25°}$ 1·5670. Bergmann *et al.* (*ibid.*) record b. p. 166—167°/15 mm. As noted by them, the sample did not take up the theoretical amount of bromine even on standing with excess.

15 C.c. were subjected to a pressure of 5000 atm. at 100° for 91 hours. The product distilled completely at 172—173°/14 mm. There was no viscous or hard residue in the flask or any

blistering on its walls, such as occurs during distillation when polymers are present. The first runnings had $n_{\mathrm{D}}^{25^\circ}$ 1·5668, and the final runnings $n_{\mathrm{D}}^{25^\circ}$ 1·5673.

αβ-*Dimethylstyrene.*—A sample synthesised from ethylmagnesium iodide and acetophenone (Klages, *loc. cit.*, p. 2641), after three fractionations, had b. p. 73°/14 mm., $n_{\mathrm{D}}^{25^\circ}$ 1·5293. 13·0 G. were subjected to 5000 atm. at 120° for 96 hours. The product distilled almost completely at 74°/14 mm., the temperature finally rising to 76°. The residue (0·3 g.) had *M*, 251 [$(C_{10}H_{12})_2$ requires *M*, 264]. Hence only 2·3% of *dimer* was obtained. It did not decolorise bromine solution in the cold.

α-iso*Propenylnaphthalene.*—α-Acetylnaphthalene was freed from the β-compound by means of the picrate (Stobbe and Lenzner, *Annalen*, 1911, **380**, 95) and converted by means of methylmagnesium iodide into α-naphthyldimethylcarbinol (Grignard, *Bull. Soc. chim.*, 1896, **25**, 497). This was dehydrated with acetic anhydride as for α-methylstyrene; the hydrocarbon had b. p. 97°/0·1 mm., $n_{\mathrm{D}}^{25^\circ}$ 1·6070 (lit.: b. p. 125°/8 mm., $n_{\mathrm{D}}^{25^\circ}$ 1·6068).

A sample was subjected to 5000 atm. at 125° for 166 hours. Over 90% of the fluid distilled below 110°/0·1 mm. The residue was dissolved in benzene, precipitated, and purified as for α-methylstyrene polymers; yield 1·9% [Found: *M*, 905].

A second sample of the monomer was subjected to 10,000 atm. at 125° for 30 hours. The product was a gum with a pale greenish fluorescence. From 2·4 g., 1·3 g. of purified and dry high *polymer* were isolated by the precipitation method used for α-methylstyrene; yield 54% [Found: *M*, 1260, 1272. $(C_{13}H_{12})_8$ requires *M*, 1344].

as-*Diphenylethylene.*—The hydrocarbon ("Organic Syntheses," **6**, 32) had b. p. 148°/15 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·6075 (lit.: b. p. 145—146°/14 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·6085). A sample was subjected to 5000 atm. for 68 hours at 120°. Distillation of the product under reduced pressure gave 64·5% of unchanged monomer (b. p. 147°/14 mm.; $n_{\mathrm{D}}^{19^\circ}$ 1·6050). The remaining material (dimeride) was distilled at 0·1 mm. and all passed over at 215—240°, the rise in temperature being steady. The distillate, a hard resin with pale bluish fluorescence, when pulverised had m. p. 100—105°. After repeated crystallisations some prisms were isolated, m. p. 118—121°. The crude *dimer* had *M*, 347, 347 [$(C_{14}H_{12})_2$ requires *M*, 360]. A similar result was obtained in an experiment for 96 hours at 150° and 5000 atm. The dimer did not decolorise bromine in chloroform.

*Ethyl Cinnamate.*—15 C.c. of redistilled ester were subjected to 4000 atm. at 125° for 240 hours. The product was a stiff, highly opalescent jelly which, when pressed on a porous tile, gave a fine white powder. This was washed several times with cold ethyl alcohol and dried in a vacuum desiccator for some weeks; yield 58·5%. Repetition of the experiment for 96 hours with addition of 0·25% of dry hydrogen chloride as catalyst did not accelerate the reaction.

iso*Amylene* (*Trimethylethylene*).—The hydrocarbon prepared by dehydrating pure *iso*amyl alcohol with 10% hydrochloric acid in a sealed tube at 100° (Michael and Zeidler, *Annalen*, 1911, **385**, 257) had, after fractionation, b. p. 36·5°/765 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·3868. Trimethylethylene has b. p. 38·4°/760 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·3878 (Norris and Reuter, *J. Amer. Chem. Soc.*, 1927, **49**, 2633). The sample prepared probably contained a small proportion of methylethylethylene.

15 C.c. were placed in a cold pressure vessel which was then closed and heated to 125°. A pressure of 5000 atm. was applied for 96 hours. The vessel was cooled,* the pressure released, and the product distilled through a jacketed glass column 12″ × 0·5″ packed with broken glass. The product distilled completely at 36·5° and there was no solid residue. The column was drained into a micro-flask, and the collected liquid distilled very slowly. All boiled at 36·5—37·0°. The experiment was repeated at 10,000 atm. for 24 hours at 125° but no polymers were formed.

$\Delta^{\gamma}$-*Butenylbenzene.*—The hydrocarbon, prepared by the action of sodium on benzyl chloride and allyl bromide (Riiber, *Ber.*, 1911, **44**, 2392), was redistilled thrice under reduced pressure. The sample used had b. p. 75°/14 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·5065 (lit.: b. p. 72—73°/13 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·5059). 15 C.c. were subjected to 5000 atm. at 125° for 78 hours. The product boiled almost entirely at 54—60°/0·1 mm., and only 2% of viscous material remained. A similar experiment at 100° for 96 hours gave the same result.

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* In all other experiments the pressure was released while the vessel was at the reaction temperature; in this instance the procedure was altered owing to the low b. p. of the *iso*amylene.