CCCCXLIX.—*Properties of Conjugated Compounds. Part XIV. An Examination of the Homogeneity of Seven Monomethyl- and Dimethyl-butadienes and the Influence of the Position of Alkyl Substitution in these Substances on Refractivity.*

By ERNEST HAROLD FARMER and FRANK LOUIS WARREN.

THE butadienoid hydrocarbons present the simplest examples of carbon conjugation; consequently an exact knowledge of their physical properties is of considerable interest in relation to current speculations concerning polarisation in the conjugated condition. Yet these substances as ordinarily prepared have proved extremely unsatisfactory for the making of precise physical measurements—not so much for the reason that chemically pure specimens have been unobtainable as that ability to demonstrate satisfactorily the homogeneity of a given preparation has been lacking. It has been the common experience of workers in this field that synthetic preparations of the individual alkylbutadienes distil over considerable but varying ranges of temperature and it has been the custom to select arbitrarily fractions of the distillate for experimental employment: in this way different workers have utilised for their observations specimens of considerably different boiling point.

An obvious explanation of the range of boiling points is to hand: four of the seven monoalkyl- and dialkyl-butadienes are theoretically capable of showing geometrical isomerism and in one instance at least (piperylene) low-boiling and high-boiling fractions have been assumed to represent *cis*- and *trans*-isomerides (Prévost, *Ann. Chim.*, 1928, **10**, 358). There has been no vestige of proof that such is the case and, indeed, there has been considerable doubt as to the capacity of *cis*- and *cis-trans* forms of simple aliphatic butadienes to possess more than a transient existence (compare the example of $\alpha\delta$-diphenylbutadiene; Straus, *Annalen*, 1905, **342**, 214); but the fact that the observed boiling point ranges of those butadienes (open-chain and cyclic) which are incapable of showing geometrical isomerism are considerably smaller than the ranges of those which can exist in more than one form lends weight to the explanation. There has been, however, only too good reason to question the *chemical* homogeneity of hydrocarbon specimens produced by the ordinary methods. All the preparative processes involve elimination or degradation reactions, frequently carried out at a high temperature, so that the formation of saturated or ethylenic by-products or even mixtures of isomeric conjugated compounds is by no means improbable. If such substances are formed in even small proportion, the prospect of removing them by fractional distillation is small.*

The authors desired to reach a definite conclusion concerning the chemical and configurational homogeneity of alkylbutadiene preparations as a necessary preliminary to investigating the effect of substitutional changes on certain of the physical properties of these substances. Extensive experience of the recorded methods of preparation showed that the range of boiling point of the different products varied too widely from method to method and changed far too seriously with modifications of the experimental conditions to admit of any general presumption of chemical homogeneity. It became necessary, therefore, to select carefully for use those methods of preparation which consistently gave the most uniform product in respect of boiling point. The procedure adopted was first to test rigidly the chemical homogeneity of the products obtained by the selected methods and secondly to examine the physical properties of the whole (*i.e.*, without any " cutting " by fractionation) of the satisfactory preparations. The conclusions drawn from the observations are set out below. The selected methods are described in the experimental portion of the paper, where reference is also made to the quality of the products obtained by certain alternative methods.

An important necessity in preparing the synthetic samples for use was thorough washing with water, since traces of the parent alcohols or their oxygenated derivatives were liable to be retained : attainment of constancy in the values for the dielectric constant, refractive index and polarisation (provided each specimen was examined as a whole and suffered no appreciable loss of any particular fraction during distillation) afforded a guide to the removal of these impurities. There was, however, the instability of the hydrocarbons also to be taken into account. All the alkylbutadienes polymerise to some extent on heating or standing and for this reason the practicability of conducting a prolonged series of accurate measurements on this group of compounds was somewhat doubtful at the outset. The difficulty arising from this cause proved, however, to be less serious than was anticipated and it was found that by scrupulously distilling the specimens *on all occasions* immediately before use and rejecting at each distillation the last few c.c. of the sample,† the polymeric material present during observations (although detectable in certain measurements) was extremely small in amount. The

---

* Tolerably pure specimens could presumably be obtained by selecting suitable fractions of narrow range of boiling point.

† For this reason, no less than for precision in fractionation, the synthesis of *large* specimens of the hydrocarbons was desirable.

peroxidic material which gradually formed on standing was also removed by this procedure.

(1) *Chemical Homogeneity.*

The direct testing of the chemical homogeneity of butadienoid hydrocarbons only recently became possible through the Diels–Alder reaction : no other additive reaction of these substances is known to give entirely crystalline products of sharp and distinctive melting point in quantitative yield. Samples of the washed and dried hydrocarbon preparations were treated with equimolecular proportions of pure maleic anhydride in benzene. Four of the seven alkylbutadienes (β-methyl-, αγ-dimethyl-, αδ-dimethyl- and βγ-dimethyl-) gave quantitative and perfectly homogeneous addition products, whilst the other three gave polymerised products under the influence of maleic anhydride. One of the latter group, αα-dimethylbutadiene, gave quantitatively under all the conditions tried a polymeric addition product of apparently high molecular weight; a second, αβ-dimethylbutadiene, polymerised to some extent (4%) under the conditions required for complete condensation, whilst the third, α-methylbutadiene, although polymerising extensively in the absence of special precautions, could be caused to combine with only small polymerisation ($< 5\%$) at 0°. The incompleteness of the formation of normal addition products in the case of α-methyl- and αβ-dimethyl-butadienes was disconcerting, but all efforts to secure complete union of the reactants while inhibiting polymerisation failed. There was no question of the inclusion in the specimens of paraffin impurities, since the total weight of non-volatile product invariably equalled that of the reactants; likewise the inclusion of aliphatic olefins or non-conjugated diolefins appeared equally to be out of the question, since these substances, so far as the authors have discovered, remain quite unaffected by maleic anhydride at 0° or room temperature (see the conditions necessary to bring about additive polymerisation of the aromatic olefins; Wagner-Jauregg, *Ber.*, 1930, **63**, 3213). The extent to which the polymerised products were formed by mere hydrocarbon polymerisation rather than by polymeric union of the hydrocarbon with maleic anhydride was not ascertained, but some non-additive polymerisation may have occurred, since minute quantities of maleic anhydride could be recovered. The authors did not, however, succeed in obtaining a quantitative yield of monomeric addition product from *any* specimen of either hydrocarbon which they handled, and since they found no unambiguous indication that the " uncut " specimens in question were other than quite pure, concluded that the observed tendency towards the formation of polymerised products was an inherent property of the material. The unpreventable and complete formation of a polymerised product in the case of the αα-hydrocarbon,* representing the same inherent property in extreme form, would seem to support the conclusion.

Variation in Physical Properties.—The range of boiling point observed with the different hydrocarbons and the manner in which the density (d), dielectric constant (ε), refractive index (n), and molar polarisation (P_2) were found to vary from fraction to fraction (progressively increasing in boiling point) of each preparation are shown in the tables which follow. The practical details relating to these measurements are included in the experimental portion (section D).

α-Methylbutadiene (*piperylene*) *fractions.*

B. p./765·7 mm.	Vol. (c.c.).	$\varepsilon^{25°}$.	$d_{4°}^{25°}$.	$n_{\mathrm{D}}^{20°}$.	P_2.
<42°	25	2·352	0·6709	1·4299	31·52
42·0—42·2	20	2·331	0·6717	1·4305	31·14
42·2—42·4	63	2·334	0·6736	1·4308	31·10
42·4—42·6	220	2·327	0·6739	1·4310	30·97
42·6—42·8	45	2·328	0·6746	1·4314	30·96

β-*Methylbutadiene* (*isoprene*). The whole of the sample (about 150 c.c.) boiled between 33·9° and 35·3° at 750 mm. This range of 1·4° appeared from careful observation of the boiling point variation to be due entirely to superheating and when the sample was separated into two fractions by distillation under a column the concordant values shown in the following table were obtained. The two fractions were recombined for subsequent use.

B. p./748 mm.	$\varepsilon^{25°}$.	$d_{4°}^{25°}$.	$n_{\mathrm{D}}^{25°}$.	P_2.
33·9—34·3°	2·098	0·6754	1·4176	27·01
34·3—35·3	2·098	0·6754	1·4177	27·01

αα-*Dimethylbutadiene.* Owing partly to the labour and expense involved in the synthesis, and partly to the accidental loss of a large quantity of material, only about 50 c.c. of the hydrocarbon were available. The specimen distilled completely within 0·5° and when separated into two fractions gave the values shown; further measurements were not made owing to the necessity of economising material.

---

* No unambiguous chemical evidence as to the αα-constitution of the hydrocarbon prepared by the (indirect) dehydration of *cyclo*propyldimethylcarbinol (p. 3232) has yet been published. Recent work of one of the authors with Mr. F. C. B. Marshall has shown that it yields acetone on degradation, and is undoubtedly a conjugated diene which is quite different from the αβ-, αγ-, αδ-, and βγ-dimethylbutadienes. Other supposed methods of preparing the αα-hydrocarbon yield the αγ-compound (compare Diels and Alder, *Annalen*, 1929, **470**, 98), save possibly that of Krestinsky (*Ber.*, 1922, **55**, 2760), which had escaped the authors' notice at the time this investigation was proceeding; the physical constants, however, recorded by Krestinsky strongly suggest that his preparation was not chemically homogeneous.

B. p./758·4 mm.*	$d_{4°}^{20°}$.	$n_D^{20°}$.
76·4—76·7°	0·7183	1·4525
76·7—76·9	0·7183	1·4525

* For the whole specimen, $\epsilon^{25°} = 2·599$; $P_2 = 39·74$.

αβ-Dimethylbutadiene fractions.

B. p./746·7 mm.	Vol. (c.c.).	$\epsilon^{25°}$.	$d_{4°}^{25°}$.	$n_D^{25°}$.	P_2.
<77·0°	30	2·416	0·7192	1·4463	36·59
77·0—78·0	30	2·430	0·7241	1·4488	36·59
78·0—78·3	30	2·442	0·7250	1·4494	36·53

αγ-Dimethylbutadiene fractions.

B. p./765 mm.	Vol. (c.c.).	$\epsilon^{25°}$.	$d_{4°}^{25°}$.	$n_D^{25°}$.	P_2.
71·0—75·2°	40	2·405	0·7075	1·4426	37·00
75·2—75·8	46	2·422	0·7136	1·4460	36·99
75·8—75·9	75	2·422	0·7142	1·4464	36·96
75·9—76·0	170	2·424	0·7141	1·4466	37·00
76·0	60	2·431	0·7144	1·4468	37·11

αδ-Dimethylbutadiene fractions.

B. p./759·3 mm.	Vol. (c.c.).	$\epsilon^{25°}$.	$d_{4°}^{25°}$.	$n_D^{25°}$.	P_2.
77·0°	30	2·200	0·7006	1·4375	33·47
77·0—78·0	30	2·216	0·7046	1·4404	33·60
78·0—79·0	60	2·217	0·7078	1·4427	33·47
79·0—80·0	55	2·217	0·7097	1·4446	33·38
80·0—81·0	75	2·210	0·7114	1·4467	33·16
81·0—81·2	45	2·202	0·7139	1·4494	32·89
81·2—81·4	10	—	0·7192	1·4514	—

βγ-Dimethylbutadiene. The whole of the sample, amounting to several litres, distilled constantly, after adequate washing, at 68·8°/750 mm. (69·0°/761·5 mm.; 69·2°/769 mm.). The range of boiling point (< 0·1°) was the smallest among the hydrocarbons studied. The values $\epsilon^{25°}$ 2·099, $d_{4°}^{25°}$ 0·7215, $n_D^{20°}$ 1·4393, P_2 30·50 were obtained and were repeatedly found to be constant from preparation to preparation and fraction to fraction of the same preparation.

Conclusions.

1. Four of the seven monomethyl- and dimethyl-butadienes (β-methyl, αγ-, αδ- and βγ-dimethyl) are definitely and directly obtainable in chemically pure condition by the selected methods. The remaining three butadienes (α-methyl-, αβ- and αα-dimethyl) are doubtless also so obtainable, but owing to the strong polymerising tendency in the presence of the testing reagent the complete purity cannot be rigidly demonstrated. All the seven compounds become impure on standing owing to polymerisation and peroxide formation.

2. Just those butadienes of the series which are theoretically incapable of showing geometrical isomerism (β-methyl-, αα- and βγ-dimethyl) are obtained by the selected methods of preparation

reasonably constant in boiling point, density, refractive index and dielectric constant—not only from preparation to preparation but from fraction to fraction of the same preparation. On the other hand, those hydrocarbons of the series which are capable of showing geometrical isomerism boil over a small or comparatively large range, but show definite gradation in density, refractive index and dielectric constant from fraction to fraction of each preparation.

3. There can be small doubt that the large range of boiling point of αδ-dimethylbutadiene is due to the presence of geometrical isomerides and the observed variation of the density, refractive index, dielectric constant and polarisation is compatible with the presence of all three of the theoretically possible forms. With respect to the samples of αβ- and αγ-dimethylbutadiene prepared by the selected methods, it is probable that one of the theoretically possible geometrical forms greatly predominates and this would be particularly expected to hold in the case of the αβ-compound, which is formed from pure tiglic aldehyde by processes proceeding at comparatively low temperatures (the boiling point range of the αβ-compound is greatly increased if the final stage of preparation is carried out at 400°); it is to be noted, moreover, that both compounds, although showing variation in the density, refractive index and dielectric constant, have a molar polarisation which is almost constant.

(2) *Influence of the Position of Alkyl Substitution on Refractivity.*

Recent investigations have shown that alteration in the number and distribution of alkyl groups attached to the conjugated chain of butadienoid compounds causes profound change in the additive mode. It is known that this change of mode applies to all the ordinary dividing addenda which have yet been studied and holds for widely differing types of butadiene compounds. Presumably the influence exerted on the additive mode is directly related—at any rate so far as the initiation of reaction is concerned—to the pre-additive polarised condition of the individual butadienoid compounds : accordingly it becomes of interest to ascertain whether any clear connexion is to be seen between the state of alkyl substitution on the one hand and such permanent physical properties as the optical refractivities and the dipole moments on the other. In a future paper the determination of the dipole moments of the monomethyl- and dimethyl-butadienes will be described : in the present paper new refractivity data relating to these hydrocarbons are recorded and discussed.

The work of Brühl, Auwers, and Eisenlohr has served to indicate that not only does a special (" conjugated ") state exist in butadienoid compounds such as those under consideration, but that this state may become enhanced or neutralised (" interrupted ") under certain conditions of substitution. Satisfactory comparison of the refractivities of the alkylbutadienes has, however, been impossible owing to the fragmentary nature of the data obtained by any one observer, the mistaken identity of certain of the hydrocarbons, the serious discrepancies existing between values from different sources, and the incompleteness of the series; in addition, there has been no certainty as to the identity and homogeneity of hydrocarbon specimens obtained by the different workers and by the different methods of synthesis. Reference may be made to the refractivity figures recently obtained by van Keersbilck (*Bull. Soc. chim. Belg.*, 1929, **38**, 205) for αα-dimethylbutadiene, which closely approach the values for this hydrocarbon obtained by the authors, and to a series of refractivity determinations made some years ago by Enklaar (*Rec. trav. chim.*, 1916, **36**, 237), which includes observations for several of the monomethyl- and dimethyl-butadienes: the derivation of the specimens, however, in the latter instances is not stated.

The Hydrocarbon Specimens.—The specimens employed were the chemically homogeneous ones described above. The boiling point ranges of those hydrocarbons of the series which are capable of showing geometrical isomerism differed somewhat from the values already recorded owing to changes in the atmospheric pressure and the diminution of material in the course of operations.* αδ-Dimethylbutadiene, owing to its large range of boiling point, was divided into lower- and higher-boiling portions, a division which presumably resulted in some measure of separation of geometrically isomeric forms.

Density and Refractive Index.—The refractive indices for the H_α, H_β, H_γ and Na_D lines are recorded in the table below, the values being accurate to four places of decimals.

Molecular Refraction and Abbé Number.—The values of MR_α, MR_D, MR_β, and MR_γ have been calculated, and by extrapolation, using the Cauchy formula, independent values of MR_∞, the molecular refraction for light of infinite wave-length (necessary for the calculation of dipole moments), have been calculated from the data for the H_α and H_γ lines and Na_D and H_β lines respectively. The Abbé number (ν) has been calculated from the formula $\nu = \frac{n_D - 1}{n_\beta - n_\alpha}$.

---

* At each distillation it was necessary to reject the first few c.c. of the distillate in order to get rid of the moisture which was unavoidably collected from the walls of the apparatus. Further loss was sustained in avoiding the inclusion of polymeric material.

Density and Refractivity of the Monomethyl- and Dimethyl-butadienes.

	B. p./mm.	$d_{4^\circ}^{20^\circ}$.	$n_{\alpha}^{20^\circ}$.	$n_{D}^{20^\circ}$.	$n_{\beta}^{20^\circ}$.	$n_{\gamma}^{20^\circ}$.	MR_{α}.	MR_{D}.	MR_{β}.	MR_{γ}.	MR_{∞} (from $\alpha\gamma$)	MR_{∞} (from βD).
α-Methyl	42·4—42·6°/766	0·6803	1·4264	1·4309	1·4429	1·4536	25·65	25·89	26·52	27·07	24·65	24·65
β-Methyl	33·9—35·3/750	0·6806	1·4165	1·4207	1·4315	1·4417	25·12	25·34	25·91	26·44	24·18	24·21
αα-Dimethyl	76·2—76·6/758·5	0·7183	1·4477	1·4525	1·4656	1·4767	30·57	30·86	31·63	32·27	29·37	29·34
αβ-Dimethyl	76·0—79·4/773	0·7279	1·4465	1·4511	1·4629	1·4734	30·10	30·37	31·05	31·75	28·93	29·01
αγ-Dimethyl	75·6—75·7/762	0·7196	1·4421	1·4467	1·4583	1·4687	30·19	30·46	31·14	31·75	29·08	29·10
αδ-Dimethyl	77·0—79·8/764	0·7108	1·4384	1·4427	1·4542	1·4643	30·24	30·60	31·28	31·88	29·24	29·23
αδ-Dimethyl	79·4—81·6/765	0·7152	1·4448	1·4493	1·4614	1·4721	30·53	30·80	$31{\cdot}51_5$	32·14	29·39	29·38
βγ-Dimethyl	68·8/750 69·0/761·5 69·2/769	0·7262	1·4352	1·4393	1·4499	1·4594	$29{\cdot}50_5$	29·75	30·37	30·92	28·49	$28{\cdot}50_5$

Discussion of Results.

The most striking feature of the results is the inequality between the molecular refractions of the lower- and the higher-boiling portion of αδ-dimethylbutadiene. This inequality, which is occasioned solely by configurational differences, is much greater than the total difference between the molecular refractions of certain of the pairs of hydrocarbons. It is important to emphasise this point, but it must be remembered in comparing the two series of αδ-values with the values for the other hydrocarbons that some of the latter also consist of mixtures of geometrical isomerides which were not separated and consequently the values recorded therefor are "average" * values.

It is clear that the marked decrease in the molecular exaltation which accompanies the replacement of an α-methyl by a β-methyl group in the monomethyl compounds (already noted by Auwers and Eisenlohr, *Ber.*, 1910, **43**, 806; *J. pr. Chem.*, 1910, **82**, 65; *Ber.*, 1921, **54**, 2999, and considered to correspond to "disturbance of conjugation") cannot be consistently traced in the combinations of α- and β-methyl groups which occur in the five dialkylbutadienes. The βγ-dimethyl compound (containing two inner- or β-alkyl groups) has the lowest exaltation of the dialkyl series, whilst the αβ- and αγ-dimethyl compounds (each containing one α- and one β-alkyl group) have almost identical values, considerably greater than that of the βγ-compound. The higher-boiling (? *cis*) portion of the αδ-compound has an exaltation practically equal to that of αα-dimethylbutadiene, but if an average value for the two fractions of the αδ-compound is taken the exaltation of the latter falls below that of the αα-isomeride. Taking this average value of the molecular refraction, the order of increasing exaltation of the isomeric dimethyl-

---

* The proportions in which the isomerides occur are of course unknown, so that the values are not strictly average values.

butadienes is $\beta\gamma < {}^*\alpha\beta < \alpha\gamma < \alpha\delta < {}^*\alpha\alpha$, as might perhaps have been anticipated, the largest increments occurring at the points in the series marked *. The constitutive (conjugative or polar) significance of the order seems very problematical, however, in view of the obviously appreciable influence on the molecular refraction of geometrical configuration; moreover the order is not maintained for the molecular dispersion, the values of which, curiously enough, for the two fractions of the αδ-compound are only slightly different.

Molecular Dispersion and Abbé Number.

Alkyl-butadiene.	$M_\gamma - M_\alpha$.	Abbé number.	Alkyl-butadiene.	$M_\gamma - M_\alpha$.	Abbé number.
α-Methyl	1·42	26·1	αγ-Dimethyl ...	1·56	27·6
β-Methyl	1·32	28·0	αδ-Dimethyl (1)	1·64	28·0
αα-Dimethyl ...	1·70	25·3	αδ-Dimethyl (2)	1·61	27·1
αβ-Dimethyl ...	1·65	27·5	βγ-Dimethyl ...	1·41	30·0

The Abbé number is stated to be a function which throws considerable light on the constitution, state of unsaturation, and the presence of conjugation in liquid organic compounds. It is considered to be particularly valuable, since the molecular weight does not enter into it (compare Bielenberg, *Z. angew. Chem.*, 1929, **42**, 972). The figures for the butadienes show depressions below the values for the corresponding non-conjugated dienes of exactly the kind to be expected. α-Methylbutadiene and αα-dimethylbutadiene show the greatest depressions and, in so far as gradations of the conjugated conditions are deducible from optical data (and have meaning), must be considered the " most conjugated " hydrocarbons of the series. On the other hand, β-methylbutadiene and βγ-dimethylbutadiene show the smallest depression. The values for the two fractions of αδ-dimethylbutadiene differ very considerably, but if these values be averaged, the hydrocarbon has an Abbé number almost identical with those of αβ- and αγ-dimethylbutadiene: then the order of increasing depression among the dialkyl compounds is $\beta\gamma < \alpha\gamma, \alpha\beta, \alpha\delta < \alpha\alpha$.

The whole of the new data emphasises the distinction between the α- and αα-compounds on the one hand and the β- and βγ-compounds on the other: there is, however, no clear connexion to be seen between the αβ-, the αγ-, and the αδ-compounds, but this may be obscured by the configurational heterogeneity of the specimens employed.

EXPERIMENTAL.

(A) *Preparation of the Hydrocarbons.*—*α-Methylbutadiene* (*$\Delta^{\alpha\gamma}$-pentadiene*). The purest product was obtained by the dehydration of Δ^{β}-penten-δ-ol vapour at about 20 mm. pressure in the presence of kaolin heated to 400° (Kyriakides, *J. Amer. Chem. Soc.*, 1914, **36**, 994). The crude hydrocarbon was collected in a glass vessel cooled in ether–carbon dioxide or liquid air.

Of other methods of preparation which were tested, mention may be made of a process developed by one of the authors in collaboration with Mr. R. S. W. Thorne (unpublished work). This consisted in the dehydration of the technical diethylcarbinol supplied by the "Sharples Solvents Corporation" and the conversion of the Δ^{β}-pentene so produced into α-methylbutadiene by successive processes of bromination and dehydrobromination. The dehydration of the carefully rectified alcohol was effected by heating at 100° with twice its volume of 50% sulphuric acid (more concentrated acid increased the yield of hydrocarbon but proved undesirable in other ways). The rectified pentene was brominated at – 20° in hexane solution, and the resulting dibromide (b. p. 178°/760 mm.) passed through a column of soda-lime electrically maintained at 500°. The method had the double advantage of being expeditious and furnishing an excellent yield of hydrocarbon, but the product was definitely inferior to that derived by the method of Kyriakides, since about 10% was low-boiling (b. p. 32—39°), the remainder distilling at 39—43°.

β-*Methylbutadiene.* The preparation of the pure hydrocarbon in reasonable quantity proved to be extremely laborious. The purest product was undoubtedly obtained by the catalytic dehydration of β-methyl-Δ^{γ}-buten-β-ol ("isoprene alcohol") in the presence of aniline hydrobromide (Kyriakides, *loc. cit.*, p. 999), but the authors could find no satisfactory way of obtaining this alcohol except from isoprene itself. Crude isoprene was therefore prepared by the decomposition of limonene ("isoprene lamp" method of Harries and Gottlob, *Annalen*, 1911, **383**, 228). The immediate product of decomposition, which contained a large proportion of trimethylethylene and other substances, was fractionated, and the portion boiling below 40° (crude isoprene) treated at – 20° with one molecular proportion of pure hydrogen bromide (Claisen and Eisleb, *Annalen*, 1913, **401**, 23). The δ-bromo-β-methyl-Δ^{β}-butene so obtained (Claisen, *J. pr. Chem.*, 1922, **105**, 65) was converted by the action of 5% potassium carbonate solution into isoprene alcohol (Mokiewski, *J. Russ. Phys. Chem. Soc.*, 1899, **32**, 207), the yield of which was raised to 60% (calculated on the crude isoprene employed) by saturating the aqueous solution with potassium carbonate and extracting it with ether. This substance distilled at 98—99°. The subsequent catalytic dehydration of the alcohol was carried out by refluxing it under a long column with aniline hydrobromide (1 g., renewed from time to time) and about six drops of concentrated hydrobromic acid (the latter was necessary to start the reaction); it proceeded slowly and did not give a quantitative yield.

A considerable amount of the hydrocarbon was also synthesised by passing the vapour of α-methyl-α-ethylethylene oxide at 15—20 mm. pressure over kaolin heated at 400° (Kyriakides, *loc. cit.*, p. 665). The quality of the product, as judged by its range of boiling point, although greatly superior to that obtained by the isoprene lamp method, was disappointing in view of the great labour involved in synthesising adequate quantities of the oxide. The isoprene obtained in this way was employed as crude isoprene in the process described above.

αα-Dimethylbutadiene (*δ-methyl-*$\Delta^{\alpha\gamma}$*-pentadiene*). For the preparation of this hydrocarbon—the supposed β-*cyclo*propylpropene of Bruylants (*Bull. Acad. roy. Belg.*, 1908, 1044; van Keersbilck, *Bull. Soc. chim. Belg.*, 1929, **38**, 205)—the recorded procedure was followed in the main. Certain modifications were, however, introduced to permit of the more rapid and economical handling of the necessary quantities of material.

cyclo*Propanecarboxylic acid.* Trimethylene bromide was converted into γ-bromobutyronitrile (Derick and Hess, *J. Amer. Chem. Soc.*, 1918, **40**, 546), and the latter into cyano*cyclo*propane (Dalle, *Bull. Acad. roy. Belg.*, 1902, 36). The cyclising process was carried out by dropping the bromo-nitrile at a fairly rapid rate (a slow rate depressed the yield) into about 3—3½ times its weight of molten caustic potash maintained at 180—190°. The potash was kept agitated throughout this process in order to present fresh surfaces to the action of the bromo-nitrile. The distillate, when dried and redistilled, gave a 60% yield of pure cyano*cyclo*propane, b. p. 135°, and a quantity of unchanged bromo-nitrile. The mixture of potash and potassium bromide contained in the reaction vessel was cooled and gradually treated with water in such a way as to promote the rapid hydrolysis of the cyclic nitrile and cyclic amide contained therein; the strong alkaline solution so obtained was then boiled for 12 hours on a sand-bath. The product, after being cautiously acidified at a low temperature, yielded by ether extraction a quantity of somewhat impure *cyclo*propanecarboxylic acid, which was separately fractionated. The main yield of pure *cyclo*propanecarboxylic acid was obtained by hydrolysing the cyclic nitrile with excess of solid potash and water in similar fashion. The total yield of acid calculated on the bromo-nitrile was usually 60%.

cyclo*Propyldimethylcarbinol.* This substance had previously been obtained from acetyl*cyclo*propane (Zelinsky, *Ber.*, 1901, **34**, 2884) and from ethyl *cyclo*propanecarboxylate (Alexejew, *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 418; Bruylants, *Bull. Acad. roy. Belg.*, 1908, 1025; Kijner and Klawikordoff, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 595). The yield in the latter case was satisfactory (75%), but the authors found that the procedure could be shortened and the yield somewhat improved (80—85%) by employing the acid chloride of *cyclo*propanecarboxylic acid, which could be rapidly and economically prepared by warming the acid with about 1½ molecular proportions of thionyl chloride and fractionating the product. The acid chloride (1 mol.), diluted with ether, was added with continuous stirring and cooling to ethereal methylmagnesium iodide (2 mols.), and the product, after standing over-night, poured on ice. The mixture was extracted four times with large amounts of ether, which were separated as efficiently as possible by decantation; the residual liquor was treated with *just sufficient* acetic acid to effect dissolution of the precipitated magnesium compound and was again extracted several times with ether. The two extracts were worked up separately, the second being freed from acetic acid by shaking with sodium carbonate solution. The carbinol obtained from both extracts boiled sharply at 123—125°/760 mm. (More than usual care was necessary in the decomposition of this Grignard reaction product; incautious treatment with water and especially too strong acidification rendered the final product quite valueless. The separate working up of the carbinol contained in the second extract was a very necessary precaution.)

Formation of the hydrocarbon. The very stable bromide described by Bruylants (*Bull. Acad. roy. Belg.*, 1908, 1027), presumably $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2Br$ (compare Bruylants and Dewael, *ibid.*, 1928, **14**, 140), was obtained directly in over 80% yield by adding *cyclo*propyldimethylcarbinol to about twice the theoretical quantity of fuming hydrobromic acid. The precipitation was complete in about 10 minutes and the bromide, after being washed and dried, boiled at 152—154°/760 mm.

Several methods of removing hydrogen bromide from this compound were tested, but owing to the great stability of the bromide the alcoholic potash method of Bruylants (*ibid.*, 1908, 1046) was ultimately adopted. This was thoroughly unsatisfactory as regards yield (the formation of the large proportion of the corresponding ethoxy-compound which was noted by Bruylants, *loc. cit.*, could not be avoided), but could be conducted on a reasonably large scale and gave a uniform hydrocarbon product.

αβ-Dimethylbutadiene (*γ-methyl-$\Delta^{\alpha\gamma}$-pentadiene*). According to a method of preparing this hydrocarbon described by Abelmann (*Ber.*, 1910, **43**, 1583), γ-methyl-Δ^{β}-penten-δ-ol, derived from tiglic aldehyde and methylmagnesium iodide, was converted into δ-chloro-γ-methyl-Δ^{β}-pentene by the action of hydrochloric acid and the latter was dehydrochlorinated by heating with quinoline. It has usually been found, however, that removal of halogen acids from halogenated compounds does not yield the conjugated hydrocarbons in a high state of purity. A method of dehydrating the methylpentenol was therefore sought.

Carefully fractionated methylpentenol, obtained in 65% yield from tiglic aldehyde and methylmagnesium iodide (b. p. 136—138°. Found: C, 71·8; H, 12·0. Calc. for $C_6H_{12}O$: C, 71·9; H, 12·1%), was passed over kaolin heated at 400° under 15—20 mm. pressure. The product contained a large proportion of low-boiling hydrocarbon, so the method was abandoned. A second method consisted in refluxing the alcohol with a small amount of aniline hydrobromide under a fractionating column. Dehydration was slow, but a much purer product was obtained. The speed of dehydration was ultimately improved by increasing the concentration of aniline hydrobromide normally used to 0·5 g. per 25 c.c. of alcohol and using a *rather large* containing flask fitted with a dropping funnel and surmounted by a long column. The temperature at the top of the column was not allowed to exceed 94° and the concentration of catalyst was kept approximately constant by adding more methylpentenol from the dropping funnel at a suitable rate. Some unchanged methylpentenol distilled with the hydrocarbon.

αγ-Dimethylbutadiene (*β-methyl-$\Delta^{\alpha\gamma}$-pentadiene*). This hydrocarbon, the supposed αα-dimethylbutadiene of Kyriakides, was conveniently and very satisfactorily prepared in large quantities by the dehydration of β-methylpentane-βδ-diol (b. p. 195—200°), the reduction product of diacetone alcohol (Kyriakides, *loc. cit.*, p. 994; compare Farmer and Scott, J., 1930, 511). The necessary quantities of the diol were obtained by the electrolytic method described by Kyriakides for the reduction of acetaldol (*loc. cit.*, p. 535).

αδ-Dimethylbutadiene (*$\Delta^{\beta\delta}$-hexadiene*) *and βγ-dimethylbutadiene.* These substances were prepared by the dehydration of ethylpropenylcarbinol at 15—20 mm. pressure in the presence of kaolin at 420—450° (Kyriakides, *loc. cit.*, p. 994) and by the catalytic dehydration of pinacol (Kyriakides, *loc. cit.*, p. 987) respectively.

(B) *Treatment of the Crude Hydrocarbons.*

The different hydrocarbon specimens were usually distilled once to remove the main bulk of unchanged alcohol or glycol and then exhaustively washed (at least 20 times) with water. In all cases the last traces of these parent substances were readily removed by washing, but the removal of traces of other oxygenated materials, *e.g.*, pinacolin from βγ-dimethylbutadiene, α-ethoxy-δ-methyl-Δ^{γ}-pentene from αα-dimethylbutadiene, and methylethylethylene oxide from isoprene, required more prolonged washing and also one or more distillations of the material under a long column in order to segregate the bulk of the impurity in the distilling flask (a few c.c. of material, representing a very small fraction of the whole, were rejected at each distillation). The hydrocarbons were dried over calcium chloride and distilled at least twice over sodium. In all cases washing operations were repeated until satisfactorily constant values of the physical properties were obtainable (see p. 3222). The washed and dried preparations were once distilled and a sample of each was submitted to the test for chemical homogeneity; subsequently, those preparations which gave a satisfactory result were carefully fractionated.

(C) *Test of Chemical Homogeneity.*

A weighed amount of the conjugated hydrocarbon (4—5 g.) was dissolved in benzene and to the solution a benzene solution of the equivalent amount of maleic anhydride was added. Since maleic anhydride had a strong polymerising action in some cases, the mixture was immediately cooled to 0° and maintained at this temperature for 12 hours. Usually the mixture was then heated at 100° in a sealed tube for several hours, after which the solvent was removed at reduced pressure and the product weighed, recrystallised and again weighed.

The addition products of β-methyl-, αγ-dimethyl-, αδ-dimethyl- and βγ-dimethyl-butadiene have already been described. The yields of these compounds obtained from the samples were quantitative: no change in melting point occurred on recrystallisation and no polymeric material (or only the most insignificant trace) could be separated therefrom.

It was essential to depart somewhat from the above-described procedure in the case of α-methylbutadiene, which suffered gross polymerisation on being heated with maleic anhydride. The solution of reactants when allowed to stand for 5 days at 0° gave good yields of addition product, but even under these conditions it was impossible to check entirely the polymerising tendency induced by the presence of the anhydride. The α-methylbutadiene derived from Δ^{β}-penten-δ-ol gave in this way a 95% yield of recrystallised 3-*methyl*-Δ^4-*tetrahydrophthalic anhydride*, which separated from light petroleum in stout needles, m. p. 61° (Found: C, 65·1; H, 6·0. $C_9H_{10}O_3$ requires C, 65·1; H, 6·0%). This anhydride yielded the corresponding free acid, m. p. 155°, when boiled with water.

Some unavoidable polymerisation also occurred during the addition of maleic anhydride to αβ-dimethylbutadiene and consequently the maximum yield of recrystallised addition product obtained from the selected sample was only 96%. This substance, 3 : 4-*dimethyl*-Δ^4-*tetrahydrophthalic anhydride*, crystallised from light petroleum in clusters of needles, m. p. 67° (Found : C, 66·8; H, 6·65. $C_{10}H_{12}O_3$ requires C, 66·65; H, 6·65%).

αα-Dimethylbutadiene gave under all the conditions tested a quantitative yield of a polymerised addition product : no trace of a simple addition product was obtained on any occasion and the completeness of the transformation is the only chemical evidence of homogeneity which the authors were able to obtain.

(D) *Variation in Physical Properties.*

The fractionations necessary for observing the change of physical properties with boiling point were carried out in pyrex flasks heated over a small free flame, a long, easily cleaned glass column of constricted rod and disc type being used, and a standardised Anschütz thermometer reading to 1/5° : in each instance the volumes of the different fractions have been stated. With regard to the measurement of density, refractive index, dielectric constant and molar polarisation it is sufficient in the present paper to give the following details. Density was determined by means of a Hartley pyknometer of 25 c.c. capacity, adjusted in a thermostat at 20·0° or 25·0°. The refractivity was measured on a water-jacketed Pulfrich refractometer, the accuracy of which was determined over the range required by the aid of standard liquids. (During the determination of the refractivity values recorded in the table, p. 3228, the room temperature differed inappreciably from the temperature of observation, 20·0°.) The dielectric constant was determined by a heterodyne method which will be fully described, along with the details of the method of determining the molar polarisation, in Part XV of this series (the degree of accuracy attained in these measurements will be considered in the same paper).

The authors' thanks are due to the Government Grant Committee of the Royal Society and to the Chemical Society for grants which have defrayed a large portion of the cost of the investigation.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7.
[*Received, October* 1*st*, 1931.]