218. *Mechanism of Polymerisation. Part I. Dimeric Tetramethylethylene.*

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THE low-molecular polymerides of mono-olefinic substances appear from the few examples which have been investigated to be composite in character, the number of isomeric forms probably increasing rapidly with increase in polymeric complexity. The structural variation amongst the isomeric products at the different polymeric stages has been insufficiently determined in any example or group of examples to allow of the mechanism of low-molecular polymeric addition being clearly recognised, and at present interest centres on the discovery of a hypothesis of addition which will account for *all* the different isomeric structures which can be shown to occur in the dimeric, trimeric, etc., products, and especially on determining the adequacy of the three reaction-mechanisms at present in the field (see Farmer, *Ann. Reports*, 1935, **32**, 250), *viz.*, those involving (i) hydrogen separation, (ii) alkyl and/or hydrogen separation (Kline and Drake, *J. Res. Nat. Bur. Stand.*, 1934, **13**, 705), and (iii) addition, loss, and migration of charged atoms or groups (Whitmore, *Ind. Eng. Chem.*, 1934, **26**, 94).

The present work began with the desire to study under the mildest possible conditions of reaction the capacity for polymerisation of a simple olefin which contained *no* hydrogen atom capable of transference in the manner envisaged by the hydrogen-separation hypothesis. Tetramethylethylene was the hydrocarbon selected, for in this example an additive mechanism analogous to that which has been postulated for ethylene, *viz.*, $CH_2{:}CH_2 + H - CH{:}CH_2 \longrightarrow CH_3{\cdot}CH_2{\cdot}CH{:}CH_2$, is impossible unless isomerisation (or equivalent structural modification) of the addendum-molecule precedes addition. As regards the probability of such isomerisation occurring independently of the polymerisation process, it is sufficient to say that the hydrocarbon possesses a very considerable degree of stability towards heat alone, although at 300° in the presence of a phosphoric oxide–silica gel catalyst tetramethylethylene and its two isomerides have been found by Laughlin, Nash, and Whitmore (*J. Amer. Chem. Soc.*, 1934, **56**, 1395) to undergo interconversion in the sense :

$$\underset{(ca.\ 3\%.)}{CMe_3{\cdot}CH{:}CH_2} \rightleftharpoons \underset{(ca.\ 61\%.)}{CMe_2{:}CMe_2} \rightleftharpoons \underset{(ca.\ 31\%.)}{CHMe_2{\cdot}CMe{:}CH_2}$$

The accumulation of alkyl groups on the ethylenic carbon atoms of tetramethylethylene might perhaps be expected to entail a predisposition towards alkyl migration, but it was hoped to avoid complications of this kind by refraining from using sulphuric acid or other strong acid as polymerising agent.

Most methods for the preparation of tetramethylethylene based on elimination reactions involve the formation of some substantial proportion of *as.*-methyl*iso*propylethylene, with possibly traces of *tert.*-butylethylene. A very satisfactory product, however, was obtained by systematic fractionation of the mixture of tetramethylethylene and *as.*-methyl*iso*propylethylene obtained by dehydration of dimethyl*iso*propylcarbinol with oxalic acid (compare Schurman and Boord, *J. Amer. Chem. Soc.*, 1933, **55**, 4930) and with this it was speedily found that the absence of a free hydrogen atom from the ethylenic carbon atoms of tetramethylethylene by no means rendered the hydrocarbon immune from polymerisation; indeed, after trials with various catalysts, boron trifluoride was selected as a suitable agent for promoting reaction at low temperatures with formation of a high yield of dimeride and lesser yields of higher polymerides.

Only the dimeric portion of the product from tetramethylethylene has been studied, and on the scale of experimentation available to us it has been possible to achieve only a partial determination of the nature of the dodecenes contained therein. Ozonolysis of the dimeric portion yielded a variety of aldehydes, ketones and acids, amongst which the following products were recognised : (I) Methyl*iso*propylacetaldehyde ($CHMe_2{\cdot}CHMe{\cdot}CHO$), (II) methyl *tert.*-butyl ketone ($CMe_3{\cdot}COMe$), (III) acetone, (IV) formaldehyde, and (V) a C_9-ketone (C_7H_{15}·COMe). In addition to these there was a quantity of a somewhat impure C_6-fatty acid, which by careful comparison of its well-crystallised derivatives with those of synthetic isomeric C_6-fatty acids of similar melting point was found to consist substantially of *dl*-methyl*iso*propylacetic acid, doubtless derived by further oxidation of the corresponding aldehyde; furthermore there was present a very small amount of an as yet unidentified C_6- or C_7-fatty acid which yielded an anilide, m. p. 109°.

The products (I) and (II) constituted by far the largest proportion (on a rough estimate at least 70%) of the total ozonolysis product, and since they are complementary to one another as regards the size of their carbon skeletons, they represented with little doubt the fission products of one and the same C_{12}-hydrocarbon, *viz.*, $CHMe_2$·CHMe·CH:CMe·CMe_3. As regards the remaining fission products it appears probable that the C_9-ketone (methyl heptyl ketone) and acetone, both present in the ozonolysis product in minor but substantial proportions, were also complementary, being derived from a hydrocarbon C_7H_{15}·CMe:CMe_2, the nature of the heptyl group in which is undetermined.* The significance of the formaldehyde present in the ozonolysis product is in considerable doubt: the amount was very small indeed, and although it may be derived from a dodecen containing the group $>C{:}CH_2$, which is present in the dimeride in very small proportion, it is equally possible that it represents merely a trace of abnormal oxidation product.

The bulk of the dimeride consists, then, of the hydrocarbon $CHMe_2$·CHMe·CH:CMe·CMe_3, and for the building up of the latter, two of the above-mentioned hypotheses (those involving mere hydrogen separation and alkyl separation in the addendum molecule) appear totally inadequate to account. The result also shows that even under conditions of polymerisation which to outward appearance are extremely mild, extensive rearrangement of the carbon skeletons involved can take place with ease. Now an important feature of Whitmore's hypothesis is that it provides a simple mechanism for a wide variety of skeletal rearrangements which, apart from the mechanism, appear to be of the most drastic character. Whitmore's hypothesis can account for the appearance of the hydrocarbon $CHMe_2$·CHMe·CH:CMe·CMe_3, and may well cover the formation of all the various dimeric forms of tetramethylethylene which appear in practice, but at present it is somewhat difficult to forecast which out of the numerous isomeric forms that are possible under the hypothesis will actually appear.

In the course of this work it has been necessary to synthesise most of the isomeric forms of hexaldehyde and to obtain three solid derivatives from each for purposes of comparison. Although many of these derivatives had previously been obtained, the melting points in a number of cases required revision. Six of the eight isomeric hexoic acids were also synthesised, but in this case no substantial differences in the melting points of their derivatives from those recorded in the literature were observed.

EXPERIMENTAL.

Tetramethylethylene.—It was essential for the purposes of the investigation to obtain this hydrocarbon quite free from its isomerides, *as.*-methyl*iso*propylethylene and *tert.*-butylethylene. Anhydrous pinacol was converted by the action of phosphorus tribromide into the corresponding dibromide (Couturier, *Ann. Chim. Phys.*, 1892, **26**, 433), and this debrominated as recommended by Thiele (*Ber.*, 1894, **27**, 455). The olefin obtained was fairly pure after several fractionations, but the yield was only 30%.

Dimethyl*iso*propylcarbinol, b. p. 117·5—119·5°/765 mm., was smoothly obtained from *iso*propylmagnesium bromide and acetone under the conditions described for the analogous preparation of methyl*iso*propylcarbinol ("Organic Syntheses," XII, 48). Dehydration by means of the catalysts employed by Henry (*Compt. rend.*, 1907, **144**, 552), Kishner and Chonin (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1770), Couturier (*Bull. Soc. chim.*, 1911, **9**, 899) and Lindner (*Monatsh.*, 1911, **32**, 421) gave mixtures of tetramethylethylene and methyl*iso*propylethylene, and so did Whitmore's modification (*J. Amer. Chem. Soc.*, 1933, **55**, 3809) of Tschugaev's well-known method (together with much polymeride). The method of Kyriakides (*J. Amer. Chem. Soc.*, 1914, **36**, 987) proved too slow for use.

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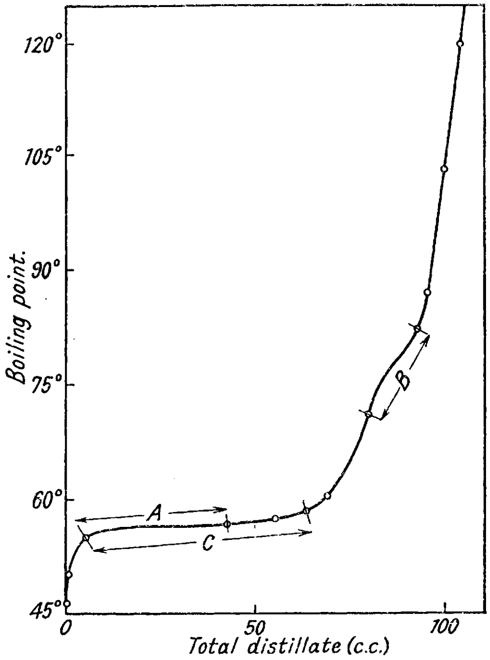
* The number of theoretically possible methyl heptyl ketones is 39, and it has not been possible to synthesise all the necessary reference compounds for identification.

Ultimately oxalic acid was used as dehydrating agent, the procedure of Schurman and Boord (*ibid.*, 1933, **55**, 4930) being followed, whereby the carbinol yielded a mixture of tetramethylethylene and methyl*iso*propylethylene, together with a little polymeric hydrocarbon. Rigorous fractionation of the mixture (b. p. 54·0—73·2°) over sodium, a jacketed Widmer column being used, gave a very satisfactory separation. From 609 g. of hexylene, 384 g. of pure tetramethylethylene, b. p. 72·9—73·2°/758 mm., were separated (Schurman and Boord give b. p. 72·9—73·2°/760 mm. for tetramethylethylene, and 55·6—56·0°/760 mm. for *as.*-methyl*iso*propylethylene; *tert.*-butylethylene boils at 40·2°/741 mm., Whitmore, *ibid.*, 1934, **56**, 1395).

To ensure further that the fraction selected contained no substantial proportion of *as.*-methyl*iso*propylethylene, the dibromide of the hydrocarbon was examined for the presence of methyl*iso*propylethylene dibromide. Accurate estimation of the yield of the camphor-like dibromide of tetramethylethylene by weighing the pure recrystallised solid was impossible owing to the excessive volatility of the latter (barely 90% survived evaporation of the solvent and crystallisation), but careful search gave less than 1% of non-volatile liquid impurity which could contain or represent the liquid dibromide of *as.*-methyl*iso*propylethylene.

Polymerisation of Tetramethylethylene.—Boron trifluoride was very effective in inducing polymerisation at low temperatures (*e.g.*, −60°), but a higher proportion of the dimeride could be obtained at somewhat higher temperatures. Several polymerisations were carried out with this catalyst, the largest of these being conducted as follows: Tetramethylethylene (150 g.) was cooled to − 10° in a 1 l. Drechsel bottle and treated with the boron trifluoride evolved from calcium borate (40 g.), calcium fluoride (80 g.), and concentrated sulphuric acid (270 c.c.). The product was kept overnight, freed by means of a water-pump from the excess of catalyst, and distilled under reduced pressure. All the polymerisate, save a small viscous residue (2·5 g.), distilled between 54°/20 mm. and 171°/2 mm. The distillate was washed with water and with aqueous alkali, dried over calcium chloride, and fractionated. The faintly yellow liquid was first separated (partly at atmospheric pressure and partly at 13 mm.) into 14 fractions, a short Vigreux column being used. The fractions were then separately distilled at atmospheric pressure under a 10-inch glass disc column, each fraction being added to the distilling flask when the lower limit of its range of boiling point was equal to the boiling point of the liquid distilling: in this way the number of fractions obtained was the same as in the previous distillation. A third fractionation was performed under reduced pressure, an asbestos-jacketed Widmer column being used, and the fourth and final fractionation again at reduced pressure, through an air-jacketed Widmer column. All four fractionations were performed very slowly, so that the reflux ratio was approximately 10 : 1, the hydrocarbon throughout being distilled over metallic sodium. In this way 128 c.c. of hydrocarbon were obtained, ranging in boiling point between 44°/12 mm. and 123°/0·4 mm., and increasing in viscosity with rise of boiling point; the last few fractions were yellowish. The boiling-point curve in the final fractionation is shown in the figure.



Distillation of dimeric tetramethylethylene at 10—12 *mm.*

Ozonolysis of the Dimeric Fraction.—Two preliminary ozonolyses, each carried out on the *whole* of the dimeric fraction obtained in a small-scale polymerisation of tetramethylethylene, indicated clearly that the dimeric hydrocarbon was heterogeneous in composition. Separate ozonolyses were accordingly carried out on portions of the low- and the high-boiling fractions (indicated by A and B respectively in the foregoing diagram) of a larger-scale polymerisation. All ozonisations were conducted at 0—10° in a fully saturated, light petroleum medium, the ozonides being obtained on removal of the solvent as faintly yellow oils; these were decomposed by warming with water.

Ozonolysis A. The fraction of the dimeride of b. p. 54·9—56·5°/12 mm. (15·3 g.) yielded, after decomposition of the ozonides, aqueous and oily layers. The former gave positive colour tests for formaldehyde and a positive iodoform reaction, but no solid derivative of acetone could be obtained.

The acidic portion of the oily layer yielded on distillation the fractions: (i) b. p. 50—172° (0·65 g.), (ii) b. p. 172—190° (1·70 g.), (iii) b. p. 190—192·5° (1·58 g.), and (iv) a small residue which contained a trace of a solid acid. Of these, (ii) yielded a crude anilide, m. p. 105—115°, and a crude amide melting indefinitely up to 117°, and (iii) yielded an amide, m. p. 121—122°, which gave on analysis figures agreeing fairly closely with those of a C_6-fatty amide (probably the hitherto unknown *dl*-methyl*iso*propylacetamide, since, of the three C_6-amides closest to 122° in melting point, the melting point of this material was definitely depressed a few degrees by two, *viz.*, by authentic *iso*butyl- and *sec.*-butyl-acetamide). This amide also formed with little doubt the chief constituent of the crude amide of fraction (ii).

The neutral portion of the oily layer had a strong camphor-like odour. It was largely or wholly ketonic, but could not be satisfactorily oxidised with sodium hypobromite.

Ozonolysis B. The fraction of the dimeride of b. p. 71—82°/11·5 mm. (4 g.) yielded, after ozonolysis and decomposition, an aqueous layer from which the dimedon of formaldehyde (m. p. 187—190°) was prepared. This layer also gave a positive iodoform reaction, but no solid derivative of acetone could be isolated.

The neutral portion of the oily layer gave on distillation a little low-boiling aldehydic material and a ketone which showed a positive iodoform reaction and possessed a similar camphor-like odour and roughly equivalent boiling point to that obtained in the foregoing ozonolysis. From each of the fractions into which the ketone was divided by distillation a 2 : 4-dinitrophenylhydrazone was obtained, the separate specimens representing in different degrees of purity essentially one compound, melting constantly at 114·5—115·5° when pure, which corresponded in composition to the 2 : 4-*dinitrophenylhydrazone* of a ketone $C_9H_{18}O$ (Found: C, 55·8; H, 6·8; N, 17·3. $C_{15}H_{22}O_4N_4$ requires C, 55·9; H, 6·9; N, 17·4%). No other pure dinitrophenylhydrazone could be isolated.

The acidic portion of the oily layer distilled almost completely at 94°/11 mm., the distillate yielding an amide which after numerous recrystallisations melted at 113·5°, but was still not entirely homogeneous. The recrystallised product nevertheless corresponded approximately in composition to an amide, $C_6H_{13}ON$, and its melting point was not depressed by admixture with the incompletely purified amide of similar melting point obtained in working up the products of the preceding ozonolysis. Although both of these amides (as the results of ozonolysis C served to confirm) with little doubt consisted substantially of *dl*-methyl*iso*propylacetamide, no synthetic specimen of the latter was available for direct comparison at this stage. From the acidic fractions an anilide, m. p. 109°, was also derived *in very small yield*, and this gave analysis figures intermediate between those required by the anilides of a C_6- and a C_7-acid. This derivative was quite different from that previously obtained (a mixture of the two melted at *ca.* 80°), but gave no depression with an anilide (as yet unidentified) of similar melting point, subsequently obtained.

Thus in both ozonolyses, in addition to traces of formaldehyde, considerable quantities of a single C_6-acid appeared to be formed, the purification of which was difficult owing to the presence of minor amounts of one or more other acids. Examination of the different fractions of the distilled acidic products indicated that this C_6-acid occurred in nearly all, and on a rough estimate represented as a fission product probably at least 70% of the dimeric fraction of the hydrocarbon. A C_9-ketone was found among the products of each of the ozonolyses A and B, but it occurred more abundantly in the latter, in which the higher-boiling fraction of the dimeride had been employed. The presence of acetone, although strongly suspected, could not at this stage be definitely confirmed.

Ozonolysis C. A portion of the dimeride (38 c.c.), collected between 54·9° and 58·5°/10·5 mm. (range C in the boiling-point curve above), was ozonised in saturated light petroleum as before. The ozonide was decomposed with 100 c.c. of water, giving a large aqueous layer (105 c.c.) and an oily layer (33 c.c.).

Both formaldehyde and acetone were present in the aqueous layer, the former undoubtedly in extremely small proportion and the latter (see below) in quite appreciable proportion. No accurate estimate, however, of either could be made owing to the presence in the aqueous layer of traces of higher aldehydes and ketones.

The combined aqueous and oily layers were steam-distilled in the presence of excess of alkali in order to drive over the neutral ozonolysis products; the alkaline residue was then acidified and again steam-distilled to remove the organic acids. The distillates were separately extracted with ether, the extracts dried over sodium sulphate, and the ether cautiously removed under a long column. The neutral and the acidic residues were each fractionated under a short column, the respective fractions shown below being collected.

Neutral ozonolysis products.

Fraction.	B. p.	Weight, g.
C1	40—60° (760 mm.)	0·2
C2	69—90 ,,	0·75
C3	90—100 ,,	1·25
C4	115—120 ,,	1·7
C5	125—140 ,,	1·4
	50—70 (20 mm.)	
C6	70—85 ,,	2·5
C7	85—90 ,,	3·1
C8	95—105 ,,	1·5
C9	Residue	1·25

Acidic ozonolysis products.

Fraction.	B. p.	Weight, g.	Equiv.
C10	24—34° (20 mm.)	0·6	
C11	75—90 ,,	0·3	
C12	90—100 (19 mm.)	1·9	117·1
C13	100—105 (18 mm.)	3·1	121·5
C14	105—111·5 ,,	1·6	126·2
C15	Residue	0·4	

The aqueous liquor left after extraction of the neutral distillate with ether was treated with 2 : 4-dinitrophenylhydrazine sulphate. The solid derivative formed, after fractional precipitation from methanol, followed by crystallisation from ether, melted at 124°. This substance was acetone-2 : 4-dinitrophenylhydrazone (m. p. 124—126°), and its amount quite appreciable. No other pure dinitrophenylhydrazone could be isolated.

Examination of neutral products. The lower fractions (C1—C3) were mainly aldehydic and underwent some oxidation to fatty acids on standing. Solid derivatives formed from the aldehydes were not homogeneous and required repeated crystallisation before constant melting points were attained.

Fraction C3 yielded the following derivatives: (1) A semicarbazone, which after one recrystallisation from methanol formed colourless needles, m. p. 142°; the amount was insufficient for further purification, but the analysis figures agreed best with those required for the semicarbazone of a C_6-aldehyde or ketone (Found: C, 54·4; H, 10·1; N, 26·0 Calc. for $C_7H_{15}ON_3$: C, 53·5; H, 9·6; N, 26·7%). (2) The 2 : 4-dinitrophenylhydrazone of a C_6-aldehyde or ketone, which after several crystallisations from light petroleum melted constantly at 124—125° (Found: C, 51·5; H, 5·47; N, 19·5. $C_{12}H_{16}O_4N_4$ requires C, 51·4; H, 5·7; N, 20·0%). Of the recorded C_6-aldehydes and ketones, only two form 2 : 4-dinitrophenylhydrazones melting in the region of 125°, *viz.*, methyl*iso*propylacetaldehyde (m. p. 123°, 124—125°) and methyl *tert.*-butyl ketone or pinacolone (m. p. 123°, 131°). Both of these substances were synthesised, and their dinitrophenylhydrazones prepared, but neither synthetic derivative had the pale yellow colour of the compound derived from the ozonolysis product: the dinitrophenylhydrazone of authentic methyl*iso*propylacetaldehyde formed orange-yellow crystals, m. p. 122° (mixed m. p. with compound from the ozonolysis product, *ca.* 100°) and that of authentic pinacolone formed orange needles, m. p. 125—131° and giving mixed m. p.'s (different mixtures) between 125° and 131°. Both the derivative from the ozonolysis product and the synthetic specimen of pinacolone dinitrophenylhydrazone, however, after melting and resolidifying, were orange in colour and melted at 131°; moreover, mixtures of the resolidified specimens melted at 131°. This behaviour accords with Whitmore and McLaughlin's discovery (*J. Amer. Chem. Soc.*, 1933, **55**, 3732) that pinacolone dinitrophenylhydrazone exists in two crystalline modifications, m. p. 125° and 131°, the former passing into the latter on melting; these authors, however, make no reference to the different colour or crystalline form of the modifications. (3) A dimedon derivative was also obtained (m. p. *ca.* 128°), but in insufficient amount for adequate crystallisation or analysis.

Fraction C4 gave a 2 : 4-dinitrophenylhydrazone, which after crystallisation formed pale yellow needles, m. p. 124°, identical with the low-melting 2 : 4-dinitrophenylhydrazone of pinacolone (m. p. 124°) obtained from fraction C3.

Fractions C5 and C6 both contained aldehydic and/or ketonic material, the former giving a positive iodoform reaction. Neither, however, could be satisfactorily oxidised with sodium hypobromite or yielded solid derivatives with 2 : 4-dinitrophenylhydrazone.

From fraction C7 an oily semicarbazone was obtained. This, when dissolved in methanol and evaporated in a vacuum desiccator, yielded crystals, m. p. 170—172° (Found: C, 60·0; H, 10·9. $C_{10}H_{21}ON_3$ requires C, 60·2; H, 10·6%). A semi-solid 2 : 4-dinitrophenylhydrazone was also obtained from the fraction. This, after draining, and crystallising alternately from dilute alcohol and light petroleum, yielded orange-yellow plates, melting constantly at 120—

121°. This derivative, although of somewhat similar m. p., was quite different from the dinitrophenylhydrazone (m. p. 125°) obtained from fractions C3 and C4, depressing the m. p. of the latter to 95°. Nevertheless, analysis showed that the dinitrophenylhydrazone was a derivative of a C_6-aldehyde or ketone ($C_6H_{12}O$) (Found : C, 51·2; H, 5·8. $C_{12}H_{16}O_4N_4$ requires C, 51·4; H, 5·8%). Of the two 2 : 4-dinitrophenylhydrazones of C_6-aldehydes and ketones having m. p.'s in the neighbourhood of 121°, *viz.*, those of pinacolone and methyl*iso*propylacetaldehyde, only that of the latter remained as a possibility, and direct comparison of the foregoing specimen with authentic methyl*iso*propylacetaldehyde-2 : 4-dinitrophenylhydrazone (m. p. 122°) showed the two to be unquestionably identical (mixed m. p. 121°).

Fraction C8 yielded an oily 2 : 4-dinitrophenylhydrazone which partly solidified on standing. The solid portion (m. p. 110—112°) after two recrystallisations from light petroleum melted at 120° and was found to be identical with the 2 : 4-dinitrophenylhydrazone obtained from fraction C7.

Acidic products of ozonolysis. These products, save for the small residue, consisted of fatty acids. Titration of representative portions of the fractions C13—C15 with *N*/10-sodium hydroxide showed that the mean molecular weight of fraction C13 corresponded to the value required for a C_6-fatty acid, and those of fractions C14 and C15 lay between those required for C_6- and C_7-acids. The experimental values, however, were likely to be rather high, owing to the presence of traces of non-acidic impurities and of higher acids (*e.g.*, a C_8-acid from the C_9-ketone formed by ozonolysis).

Solid derivatives were prepared, *via* the acid chloride, only from the largest fraction, C13. The amide melted at first at 106—109°, but after five recrystallisations its m. p. was still several degrees below that of pure *dl*-methyl*iso*propylacetamide (m. p. 128—130°), synthesised for the comparison, although it was sufficiently pure to leave no doubt as to its identity with the latter.*

The anilide was obtained as an oil, which, when taken up in light petroleum, partly solidified. The bulk of the solid melted at 80—85°, but it was heterogeneous. A little of an apparently homogeneous anilide, m. p. 107—109°, was isolated, and direct comparison showed that this was neither *iso*butylacetanilide (m. p. 112°) nor *iso*valeranilide (108—111°); it resembled, however, and gave no depression of m. p. with, the anilide, m. p. 109°, isolated in ozonolysis B (p. 1042); moreover, it appeared from its composition to be the anilide of a C_7- rather than of a C_6-acid (Found : C, 76·4; H, 9·1. $C_{12}H_{17}ON$ requires C, 75·4; H, 9·0%. $C_{13}H_{19}ON$ requires C, 76·0; H, 9·3%). The major portion of the solid, however, was not resolved into its components, and rather remarkably no methyl*iso*propylacetanilide was isolated in a reasonably pure condition.

The *p*-toluidide was obtained as an oil, a small proportion of which solidified after distillation. This portion, after crystallisation successively from light petroleum and dilute methanol, melted at 128·5—130·5°, but was not identified.

Isomeric Hexaldehydes.—Six of the eight theoretically possible hexaldehydes have been synthesised for purposes of comparison, although only one of these (*dl*-methyl*iso*propylacetaldehyde) was hitherto unknown. The m. p.'s of the new derivatives and the amended m. p.'s of known derivatives (where these were found to be inaccurate) are shown in the table in heavy type. Brief details of the synthetical methods found to be most satisfactory are given below.

Aldehyde.	Formula.	B. p.	2 : 4-Dinitrophenylhydrazone, m. p.	Semicarbazone, m. p.	Dimedon derivative, m. p.
n-Hexaldehyde	$CH_3\cdot[CH_2]_4\cdot CHO$	131°	104°	114·5—115·5° (106)	108·5°
Methylpropyl-acetaldehyde	$CHMePr\cdot CHO$	119—121	103	100—102	—
*iso*Butyl- ,,	$CHMe_2\cdot[CH_2]_2\cdot CHO$	121	**99**	**126·5—127·5**	**133**
sec.-Butyl- ,,	$CHMeEt\cdot CH_2\cdot CHO$	—	**93·5—94·5**	128—129	**144**
dl-Methyl*iso*propyl- ,,	$CHMe_2\cdot CHMe\cdot CHO$	**115—117**	**123—123·5**	**110—111**	**162**
l- ,, ,, ,,	,,		124—125	128—129 *	—
Diethyl- ,,	$CHEt_2\cdot CHO$	117—119	**94·5—95**	**97·5—99·5**	**102—102·5**
Dimethylethyl- ,,	$CMe_2Et\cdot CHO$	102—104	**145**	154—156	**118—120**
tert.-Butyl- ,,	$CMe_3\cdot CH_2\cdot CHO$	102—104	147—147	—	167

* Inactive racemised form, m. p. 109—110°.

iso*Butylacetaldehyde.* The general method of aldehyde synthesis described by Wood and Comley (*J. Soc. Chem. Ind.*, 1923, **42**, 429T) worked well in this case. To an ethereal solution of

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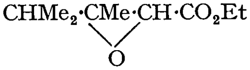
* In the earlier stages of the purification, identification with *iso*butylacetamide (m. p. 118—119°) appeared a possibility, since mixtures of *iso*butylacetamide and methyl*iso*propylacetamide show no marked depression of m. p.

*iso*amylmagnesium bromide, formed from magnesium (2/3 mol.) and primary *iso*amyl bromide (2/3 mol.), an ethereal solution of ethyl orthoformate (1/3 mol.) was gradually run in at a rate which promoted gentle refluxing. This operation took 20 minutes, and refluxing was continued for a further 2 hours, a white precipitate separating. The bulk of the ether was distilled off, and the liquid residue (resolidifiable on cooling) kept overnight and decomposed by ice-water. The diethylacetal of *iso*butylacetaldehyde, $CHMe_2·[CH_2]_2·CH(OEt)_2$, so obtained, boiled at 105—110°/18 mm., but mainly at 107·5°/18 mm. (Tschitschibabin, *Ber.*, 1904, **37**, 188, gives b. p. 180—182°). Yield, 86%. The acetal (20 c.c.), heated to 120° with 5*N*-sulphuric acid (60 c.c.), gave the aldehyde, which was purified through its bisulphite compound. The thoroughly dried, distilled aldehyde yielded the 2 : 4-dinitrophenylhydrazone in golden-yellow prisms, m. p. 99°, from light petroleum (Found : C, 51·8; H, 5·3. Calc. for $C_{12}H_{10}O_4N_4$: C, 51·4; H, 5·8%), the semicarbazone in lustrous plates, m. p. 126·5—127·5°, from methanol (Found : C, 53·4; H, 9·4. Calc. for $C_7H_{15}ON_3$: C, 53·5; H, 9·6%), and the dimedon in lustrous crystals from dilute methanol, m. p. (before and after sublimation) 133° (Found : C, 73·0; H, 9·2. Calc. for $C_{22}H_{34}O_4$: C, 72·85; H, 9·5%).

sec.-*Butylacetaldehyde.* The method of Stephen (J., 1925, **127**, 1874), starting from *sec.*-butylacetamide, and the method of Sabatier (*Compt. rend.*, 1912, **154**, 561), depending on the catalytic reduction of *iso*butylacetic acid, gave poor results. Distillation of the mixed barium salts of *sec.*-butylacetic acid (p. 1046) and formic acid furnished an oily aldehyde, which was dried, distilled, and converted into its bisulphite compound. The regenerated aldehyde gave a 2 : 4-*dinitrophenylhydrazone*, which separated in pale golden-yellow crystals, m. p. 93·5—94·5°, from light petroleum (Found : C, 50·7; H, 5·6. $C_{12}H_{16}O_4N_4$ requires C, 51·4 ; H, 5·8%), and a semicarbazone, crystallising from light petroleum in colourless prisms, m. p. 128° (Stevens, *J. Amer. Chem. Soc.*, 1935, **57**, 1115, gives m. p. 128—129°). The dimedon derivative (too small in amount for analysis) crystallised from methanol in colourless prisms, m. p. (unsharp) 144°, unchanged by sublimation.

dl-*Methyl*iso*propylacetaldehyde.* The mixed barium salt method gave an unsatisfactory result.

(1) Methyl *iso*propyl ketone [b. p. 94°/740 mm.; 2 : 4-dinitrophenylhydrazone, m. p. 122—122·5° (Allen, *J. Amer. Chem. Soc.*, 1930, **52**, 2955, gives m. p. 117°); semicarbazone, m. p. 112—113° (Bardan, *Bull. Soc. chim.*, 1931, **49**, 1875, gives m. p. 112°)], obtained in good yield by the method of Whitmore, Evers, and Rothrock ("Organic Syntheses," **13**, 68), was converted into ethyl β-methyl-β-*iso*propylglycidoacrylate,  $CHMe_2·\underbrace{CMe·CH}_{O}·CO_2Et$ by Rutovski and Daiev's procedure (*Ber.*, 1931, **64**, 697) for preparing glycidic esters. The interaction between the ketone and ethyl chloroacetate in presence of sodium proceeded smoothly, the product yielding much unchanged chloroacetic ester and a slightly yellowish-green oil, b. p. 203—213°. The latter (10 g.), consisting essentially of the glycidic ester, was mixed with a solution of sodium ethoxide (1·34 g. of sodium; 20 g. of alcohol), and the product treated dropwise with a little water (1·05 g.). The hydrolysis of the ester, thus begun, was completed on a steam-bath overnight. The alkaline hydrolysis product was steam-distilled to remove alcohol and unchanged ester, and then treated with excess of sulphuric acid. The acid product was heated to boiling to decompose the free glycidic acid and then steam-distilled. The hitherto unknown dl-*methyl*iso*propylacetaldehyde* passed over and was further purified by conversion into its sodium bisulphite compound. The regenerated aldehyde, b. p. 115—117°/770 mm., yielded a 2 : 4-*dinitrophenylhydrazone*, m. p. 121—123·5° (Found : C, 52·0; H, 5·8. $C_{12}H_{16}O_4N_4$ requires C, 51·4; H, 5·75%), a *semicarbazone*, m. p. 110—111° (Found : C, 53·5; H, 9·4. $C_7H_{15}ON_3$ requires C, 53·5; H, 9·6%),* and a *dimedon*, m. p. 162° (Found : C, 72·7; H, 9·6. $C_{22}H_{34}O_4$ requires C, 72·85; H, 9·5%).

(2) Methyl*iso*propylacetic acid, b. p. 100—103°/14 mm., was esterified with alcoholic sulphuric acid, the pleasant-smelling ethyl ester boiling at 149—153°/760 mm. (Gorski, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 168, gives b. p. 148—150°/745 mm.). This ester (8·5 g.), dissolved in absolute alcohol (34 c.c.), was reduced by addition of sodium (8·1 g.) at a rate sufficient to sustain gentle ebullition. The product was kept at 120—165° for 4 hours, cooled, and decomposed by water. The resulting clear liquor was steam-distilled until it became cloudy through

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* Reindel and Kipphan (*Annalen*, 1932, **493**, 181) have obtained *l*-methyl*iso*propylacetaldehyde by the ozonolysis of ergosterol, which yields a *l*-2 : 4-dinitrophenylhydrazone, m. p. 124—125°, and a *l*-semicarbazone, m. p. 128—129°. Racemisation of the *l*-semicarbazone gave an inactive derivative, m. p. 109—110° (Guiteras, *Annalen*, 1932, **494**, 116).

precipitation of *iso*hexyl alcohol. The latter was extracted with ether, dried (anhydrous sodium sulphate), recovered (2 g.), and oxidised by potassium dichromate and sulphuric acid. The escaping methyl*iso*propylacetaldehyde was collected, dried, and used for the formation of the derivatives described in (1).

Diethylacetaldehyde. Diethylcarbinol, b. p. 114—117°/755 mm., was converted into bromodiethylmethane by means of hydrobromic acid (*d* 1·49), and the bromo-compound, after purification in the usual way (b. p. 116—122°/756 mm.), dried by distillation over potassium carbonate. By interaction of this bromide with magnesium and ethyl orthoformate the diethylacetal of diethylacetaldehyde was formed (compare p. 1045). The crude acetal gave on distillation the fractions, (i) b. p. 60—80°/16 mm., (ii) 80—90°/15 mm., (iii) 90—125°/14 mm., and (iv) b. p. above 125°/14 mm., of which (ii) consisted of almost pure acetal and gave a good yield of aldehyde on hydrolysis. The latter was converted into its bisulphite compound, and the regenerated aldehyde used directly in forming derivatives. The 2 : 4-*dinitrophenylhydrazone* formed pale orange plates, m. p. 94·5—95°, from light petroleum (Found : C, 51·5; H, 5·3. $C_{12}H_{16}O_4N_4$ requires C, 51·4; H, 5·7%), the semicarbazone, colourless prisms, m. p. 97·5—99·5°, from benzene–light petroleum (Sou Phou Ti, *Compt. rend.*, 1931, **192**, 462, gives m. p. 95°) (Found : C, 53·9; H, 9·4. Calc. for $C_7H_{15}ON_3$: C, 53·5; H, 9·6%), and the *dimedone*, colourless prisms from methanol, m. p. 102—102·5° (Found : C, 73·0; H, 9·2. $C_{22}H_{34}O_4$ requires C, 72·9; H, 9·5%).

Dimethylethylacetaldehyde. This aldehyde was not formed by interaction of *tert.*-amylmagnesium chloride with orthoformic ester, but a small yield was obtained by interaction of the same Grignard reagent with ethyl formate.

Favorski (*J. Russ. Phys. Chem. Soc.*, 1918, **50**, 43; *Centr.*, 1923, III, 667) records having obtained *tert.*-amylcarbinol from the latter two reactants, but gives no details of the reaction. Normally the diamyl derivative $(CMe_2Et)_2CH{\cdot}OH$ might be expected to arise, but Bouveault (*Compt. rend.*, 1904, **138**, 1108), through an analogous reaction between *tert.*-butylmagnesium chloride and methyl formate, conducted at − 10° to − 15°, reports having obtained *tert.*-butylcarbinol together with a small quantity of *tert.*-butylacetaldehyde.

The Grignard reagent was formed from 20 g. of *tert.*-amyl chloride and 5 g. of magnesium, 0·2 c.c. of ethyl bromide being used to start the reaction (iodine for this purpose is unsatisfactory). To it, cooled in ice-salt, 6 g. of freshly purified ethyl formate (b. p. 54·5°/773 mm.) were added. The white addition compound was left over-night, decomposed with water, and worked up in the usual way. The product was distilled and collected in four fractions, (i) b. p. 44—108°, (ii) b. p. 108—120°, (iii) b. p. 124—140°, and (iv) b. p. 160—168°. Fraction (i) contained free dimethylethylacetaldehyde : from this were obtained (1) a pale orange 2 : 4-*dinitrophenylhydrazone*, m. p. 145° after two recrystallisations from light petroleum (Found : C, 51·6; H, 5·3. $C_{12}H_{16}O_4N_4$ requires C, 51·4; H, 5·75%), (2) a semicarbazone, m. p. 153·5° (Favorski, *loc. cit.*, gives 154—156° as the m. p. of dimethylacetaldehydesemicarbazone), and (3) a *dimedone*, m. p. 118—120° after crystallisation from dilute methanol (Found : C, 72·5; H, 9·2. $C_{22}H_{34}O_4$ requires C, 72·85; H, 9·45%). Fraction (ii) yielded 2 g. of *tert.*-amylcarbinol.

Isomeric Hexoic Acids.—Of the eight isomeric hexoic acids, six were synthesised for purposes of comparison by the excellent method of Hommelen (*Bull. Soc. chim. Belg.*, 1933, **42**, Nos. 5—6). From these the required amides and anilides were readily obtained in pure condition, the m. p.'s not differing substantially from those recorded by Hommelen. For derivatives of *n*-hexoic acid and methylpropylacetic acid, the m. p.'s given by Beilstein (" Organische Chemie ") and by Hommelen respectively were accepted.

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