264. *α-Methylenic Reactivity in Olefinic Systems. Part IV. The Structure of the Dimeride formed by the Stannic Chloride-catalysed Polymerisation of Trimethylethylene. Synthesis and Characterisation of Isomeric Methyl Hexyl Ketones.*

By John W. Baker.

The " methyl hexyl ketone " obtained by ozonolysis of the stannic chloride-induced dimerisation of trimethylethylene (Baker, Part II, *J.*, 1945, 724) has been separated into two isomeric ketones, (1) giving a semicarbazone, m. p. 173°, and (2) giving a semicarbazone, m. p. 154°. The identity of the former with 4 : 4-dimethyl-*n*-hexan-2-one has been established, thus confirming the presence of a dimeride of structure $\mathrm{CHMe{:}CMe{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2Me}$ (I) derived by an addition $\overset{-}{\mathrm{S}}\mathrm{nCl_4}{-}\overset{\curvearrowright}{\mathrm{CHMe}{-}}\mathrm{CMe}{=}\overset{\curvearrowright}{\mathrm{CH_2}}\ \mathrm{Me_2C}{=}\overset{\curvearrowright}{\mathrm{CHMe}}\ \overset{+}{\mathrm{H}}$ which parallels, in the olefin system $\mathrm{H}{-}\overset{\curvearrowright}{\mathrm{C}}{-}\mathrm{C}\overset{\curvearrowright}{=}\mathrm{C}$, the Michael type of addition of the system $\mathrm{H}{-}\overset{\curvearrowright}{\mathrm{C}}{-}\mathrm{C}\overset{\curvearrowright}{=}\mathrm{O}$, to a $\mathrm{C{=}C}$ centre.

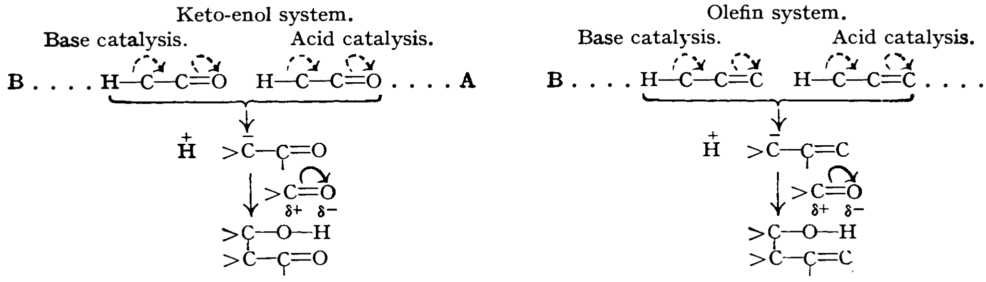
Of the remaining 16 isomeric methyl hexyl ketones, 9 have been synthesised and characterised and a further 5 are described in the literature, and none of these is identical with the second ozonolysis ketone (semicarbazone, m. p. 154°) which must therefore possess the structure $\mathrm{Me{\cdot}CO{\cdot}CHMeBu^t}$ or $\mathrm{Me{\cdot}CO{\cdot}CH_2{\cdot}CH_2Bu^t}$. Attempts to synthesise both these ketones have proved unsuccessful. Either structure would necessitate considerable skeletal change in the trimethylethylene during dimerisation, and the implications of these results on the dimerisation of tetramethylethylene (Brunner and Farmer, *J.*, 1937, 1039) are briefly discussed.

THE object of this series of investigations is to ascertain to what extent an olefinic system $\mathrm{H}{-}\overset{\curvearrowright}{\mathrm{CH_2}{-}}\mathrm{CR}\overset{\curvearrowright}{=}\mathrm{CR_2}$, activated by hyperconjugation, can undergo reactions of the types exhibited by the system $\mathrm{H}{-}\overset{\curvearrowright}{\mathrm{CH_2}{-}}\mathrm{CR}\overset{\curvearrowright}{=}\mathrm{O}$ (cf. Part I, *J.*, 1944, 296).

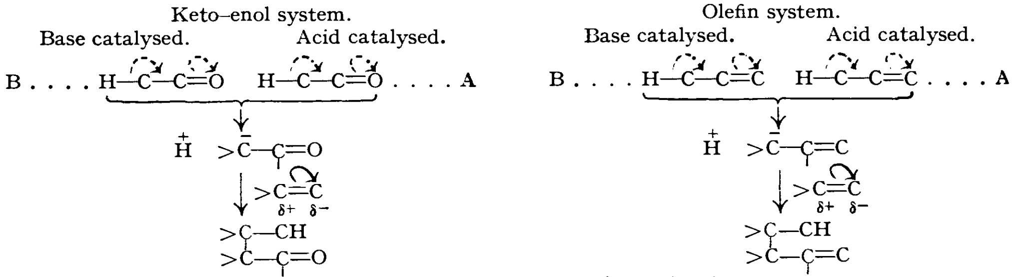
An essential feature of the latter system is its capacity to add, as the ionic fragments $\overset{+}{\mathrm{H}}\ \overset{-}{\mathrm{C}}\mathrm{H_2}{-}\mathrm{CR{=}O}$, to carbonyl, $\mathrm{C{=}O}$, and olefinic, $\mathrm{C{=}C}$, centres in the well-known aldol and Michael reactions. If the olefinic system can behave as the weak conjugate acid of the strong carbanion base $\overset{-}{\mathrm{C}}\mathrm{H_2}{-}\mathrm{CR{=}CR_2}$ analogy suggests that it might undergo additive reactions of essentially the same types. The comparison is summarised in the scheme on p. 1303.

The catalyst has a dual function : (i) to assist the removal of the (ionising) proton and (ii) to increase the polarisation of the unsaturated centre so as to activate it towards nucleophilic attack (cf. Baker and Rothstein, " Handbuch der Katalyse," Vol. II, Vienna, 1940, p. 168). In the keto–enol system basic catalysis is the more effective, first because it operates by direct attack on the ionising hydrogen and secondly because the resulting carbanion already contains, in its carbonyl oxygen atom, a suitable seat for the anionic charge $\overset{-}{\mathrm{C}}\overset{\curvearrowright}{-}\mathrm{C}\overset{\curvearrowright}{=}\mathrm{O} \longleftrightarrow \mathrm{C}\overset{\curvearrowleft}{=}\mathrm{C}\overset{\curvearrowleft}{-}\overset{-}{\mathrm{O}}$

(A) *Aldol type* :

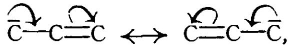


(B) *Michael type* :



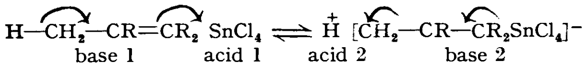
(A = acid catalyst; B = basic catalyst.)

this ion thus possessing considerable resonance stabilisation. In the analogous olefin system the anionic charge must reside on the much less electronegative element carbon,



$$\bar{C}—C{=}C \longleftrightarrow C{=}C—\bar{C},$$

unless the catalyst can accept the electron pair and so provide a more stable seat for it. It would therefore be expected that the most effective type of catalyst for parallel olefin additive reactions would be non-hydrogen *acids*, such as stannic chloride, boron trifluoride, etc., functioning in the manner already indicated in Part II (*J.*, 1945, 725), *viz.* :



$$\underset{\text{base 1}}{H—CH_2—CR{=}CR_2}\ \underset{\text{acid 1}}{SnCl_4} \rightleftharpoons \underset{\text{acid 2}}{\overset{+}{H}}\ \underset{\text{base 2}}{[CH_2—CR—CR_2SnCl_4]^-}$$

Olefin additions of type (A), *i.e.*, to C=O, have already been described in Parts I and II (*locc. cit.*). This communication deals with an addition of type (B) to C=C, *viz.*, the self-addition or dimerisation of trimethylethylene.* As indicated in Part II (*loc. cit.*, p. 727) fractionation of the polymerisation products isolated as by-products during the study of the stannic-chloride-catalysed reaction of trimethylethylene with phenyl *iso*cyanate gave three main fractions, the one of lowest b. p. (~55°/15 mm.) consisting essentially of a dimeride $C_{10}H_{20}$. Repeated fractionation of this led to the isolation of a fraction of constant b. p. 46°/12 mm. This on ozonolysis gave, as the volatile product, only acetaldehyde, identified as its *p*-nitrophenylhydrazone, 2 : 4-dinitrophenylhydrazone, and dimedon compound, indicating a =CHMe end group. No trace of formaldehyde or other carbonyl compound derived from any different end group could be detected in any experiment, including one in which the dimeride fraction employed was prepared by direct stannic chloride polymerisation of a different, carefully fractionated specimen of trimethylethylene in the absence of any complicating phenyl *iso*cyanate. This dimeride gave products identical with those obtained from the dimeride isolated as a by-product in the phenyl *iso*cyanate experiments. The other fraction of the molecule was a mixture of two isomeric methyl hexyl ketones, which were separated by fractional crystallisation of the semicarbazones into two pure semicarbazones, m. p. 173° and 154°, both of which have the composition $C_9H_{19}ON_3$. The former has now been proved by direct comparison to be the semicarbazone of 4 : 4-dimethyl-*n*-hexan-2-one (II) and thus the ambiguity reported in the preliminary investigation (Part II, p. 727) has been removed. The proved structure of this ketone means that the structure of one of the dimerides must be (I), derived by a type B addition of one molecule of trimethylethylene to a second molecule, the double

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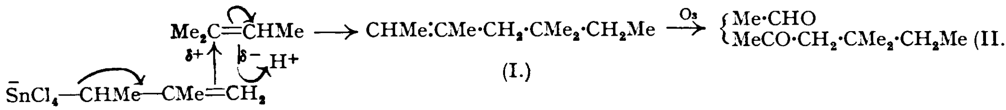
* A short summary of some of these results was published earlier (*Nature*, 1948, **161**, 171).

bond of which is polarised in the normal direction imposed by the greater electron-repulsion of the *gem*-dimethyl grouping :



The expected " Michael " type of addition in the olefin has thus been realised.

Regeneration of the ketone from the second semicarbazone, m. p. 154°, gave a liquid of a strong camphoraceous odour, b. p. 66°/60 mm., which has not been obtained in quantity sufficient to carry out a systematic degradation. Accordingly an attempt was made to formulate the structures of the various methyl hexyl ketones which would be derived from dimerisation of trimethylethylene, its prototropic isomers, $CH_2{:}CMe{\cdot}CH_2Me$ and $CH_2{:}CH{\cdot}CHMe_2$, and even a possible impurity $CHMe{:}CHEt$, by all reasonable mechanisms, including possible pinacolic rearrangements, but excluding those dimerides which did not contain the necessary $\dot{=}CHMe$ end grouping. It was soon found that several different possible mechanisms would give rise to identical structures for the dimeride and that the more probable structure of the unknown methyl hexyl ketone would seem to be one of the Nos. 1—7 of Table I.

Examples of the types of dimerisation giving rise to the various methyl hexyl ketones in Table I are given in Table II. All the ketones listed in Table I have been synthesised and characterised and none of them is identical with the unknown methyl hexyl ketone which gives the semicarbazone, m. p. 154°.

TABLE I.

No.	$Me{\cdot}CO{\cdot}C_6H_{11}$.	Melting point of 2 : 4-dinitrophenylhydrazone.	Melting point of semicarbazone.	Mixed m. p. with semicarbazone, m. p. 154°.
1.	$Me{\cdot}CO{\cdot}CH_2{\cdot}CHMePr^i$	71°	162°	147—150°
2.	$Me{\cdot}CO{\cdot}CMe_2Pr^i$	—	153	139—140
3.	$Me{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Pr^i$	76	153—155	126—140
4.	$Me{\cdot}CO{\cdot}CHMe{\cdot}CHMeEt$	—	141	124—138
5.	$Me{\cdot}CO{\cdot}CHMe{\cdot}CH_2Pr^i$	55	115	103—108 (indefinite)
6.	$Me{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CHMeEt$	67	138·5	110 (indefinite)
7.	$Me{\cdot}CO{\cdot}CH_2{\cdot}CHMePr^n$	54	108	101
8.	$Me{\cdot}CO{\cdot}CHEtPr^n$	62—64	81	70—80
9.	$Me{\cdot}CO{\cdot}CHEtPr^i$	—	121·5	105—120
	Ozonolysis ketone, $Me{\cdot}CO{\cdot}C_6H_{13}$	82	154	—

References :

(2) Locquin and Leers, *Compt. rend.*, 1924, **179**, 55; *Bull. Soc. chim.*, 1926, [iv], **39**, 436.
(3) Heilbron and Thompson, *J.*, 1929, 888 : Locquin and Heilmann, *Bull. Soc. chim.*, 1929, [iv], **45**, 875; Wieland, *Ber.*, 1925, **58**, 2015.
(4) Powell and Secoy, *J. Amer. Chem. Soc.*, 1931, **53**, 768.
(7) Clarke, *Amer. Chem. J.*, 1908, **30**, 93; *Ber.*, 1907, **40**, 353.
(8) Clarke and Riegel, *J. Amer. Chem. Soc.*, 1912, **34**, 679.
(9) Clarke, *ibid.*, 1908, **39**, 577.

The ketones in Table I were synthesised in accordance with the following schemes :

(1) $Me{\cdot}CO{\cdot}CH_2{\cdot}COMe + 2MgPr^iBr \longrightarrow Me{\cdot}\underset{\text{O·MgBr}}{C}{:}CH{\cdot}C(OH)MePr^i \longrightarrow Me{\cdot}CO{\cdot}CH_2{\cdot}C(OH)MePr^i \longrightarrow$
$Me{\cdot}CO{\cdot}CH{:}CMePr^i$ (or isomer) $\xrightarrow{Pt\text{-}H_2}$ (1).

(2) $CMe_2{:}CH{\cdot}COMe + Br_2 \longrightarrow CMe_2Br{\cdot}CHBr{\cdot}COMe \xrightarrow{\text{piperidine}} CMe_2{:}CBr{\cdot}COMe \xrightarrow{\text{NaOAc}}$
$CMe_2{:}C(OAc){\cdot}COMe \xrightarrow{10\%\ H_2SO_4} CHMe_2{\cdot}CO{\cdot}COMe$ (Dufraisse and Moureu, *Bull. Soc. chim.*, 1927, [iv], **41**, 855; Pauly and Leick, *Ber.*, 1900, **33**, 503) $\xrightarrow{2MgMeI} CMePr^i(OH){\cdot}CMe_2(OH) \xrightarrow{\text{Conc. }H_2SO_4}$
$Me{\cdot}CO{\cdot}CMe_2Pr^i$ (Locquin and Leers, *loc. cit.*).

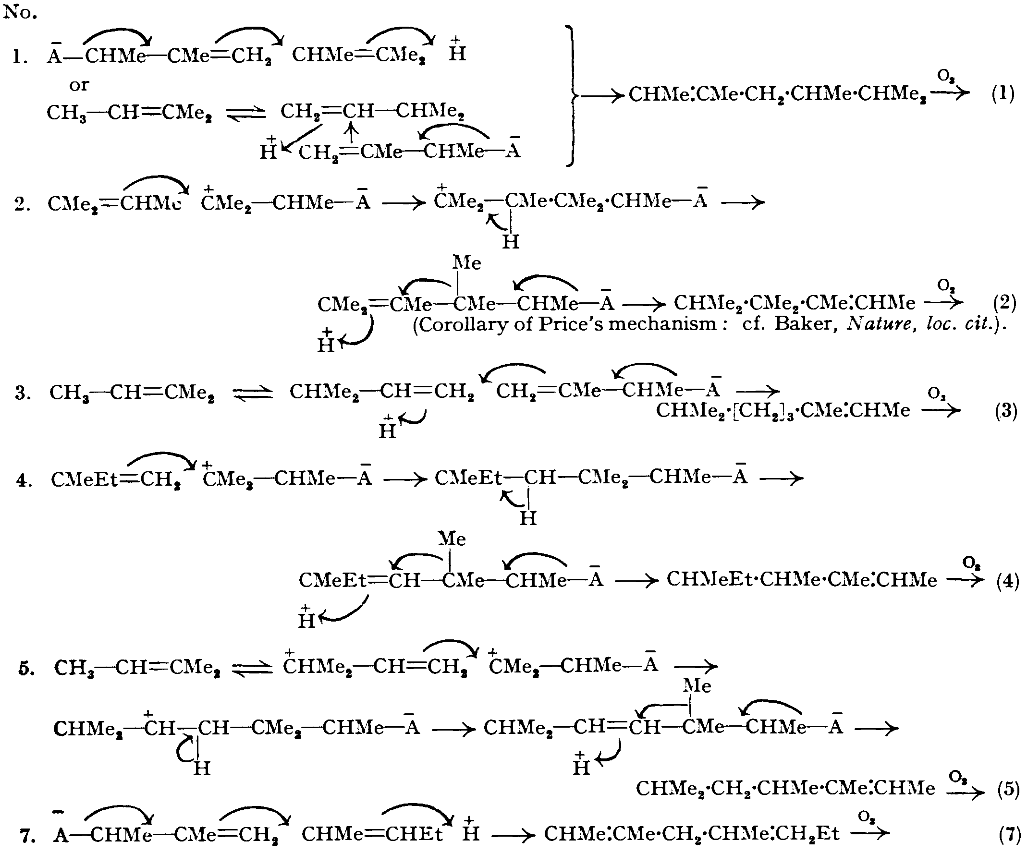
The remaining ketones were synthesised by the usual acetoacetic ester syntheses from the appropriate alkyl bromide–acetoacetic ester pair, concentrated hydrochloric acid being used for hydrolysis of the alkylacetoacetic ester. As the m. p. and the mixed m. p. of their semicarbazones show, none of these ketones is identical with the second ozonolysis ketone. Of the seventeen theoretically possible isomerides of methyl hexyl ketone, nine were thus synthesised whilst a tenth is 4 : 4-dimethyl-*n*-hexan-2-one (II), already proved to be identical with the other ozonolysis ketone giving a semicarbazone, m. p. 173°. Of the remaining seven the following five are described in the literature :

10. $Me\cdot CO\cdot[CH_2]_5\cdot Me$ (123°) (Michael, *J. Amer. Chem. Soc.*, 1919, **41**, 417; Bouveault and Locquin, *Bull. Soc. chim.*, 1904, [iv], **31**, 1157).
11. $Me\cdot CO\cdot CHMeBu^n$ (82°) (Powell, *J. Amer. Chem. Soc.*, 1924, **46**, 2516).
12. $Me\cdot CO\cdot CMe_2Pr^n$ (119·5°) (Locquin and Leers, *Compt. rend.*, 1924, **178**, 2097; *Bull. Soc. chim.*, 1926, [iv], **39**, 433).
13. $Me\cdot CO\cdot CH_2\cdot CHEt_2$ (141—142°) (Kon, *J.*, 1921, **119**, 822).
14. $Me\cdot CO\cdot CMeEt_2$ (168°) (Nybergh, *Ber.*, 1922, **55**, 1962).

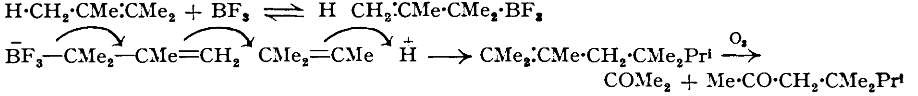
Unless the recorded melting points of their semicarbazones (given in parentheses) are seriously in error, none of these is identical with the second ozonolysis ketone. The only remaining possible structures of the latter are therefore $Me\cdot CO\cdot CHMeBu^t$ (15) or $Me\cdot CO\cdot CH_2\cdot CH_2\cdot Bu^t$ (16). Unfortunately both these are difficult to synthesise since the most obvious method, the acetoacetic ester synthesis, involved the alkylation of ethyl methylacetoacetate with a *tert.*-butyl halide (for 15) or of ethyl acetoacetate with a *neo*pentyl halide (for 16), both of which, as the work of Hughes, Ingold, and their collaborators has demonstrated, would be subject to very strong steric hindrance. Nor could this difficulty be evaded by attempting the condensation under conditions favourable to a unimolecular mechanism since, for (16) this would involve rearrangement of the *neo*pentyl group to *tert.*-amyl, and the resulting ketone would then be (II). An attempt was made to effect forced condensation of *tert.*-butyl bromide with ethyl methylacetoacetate in concentrated alcoholic sodium ethoxide in a sealed tube at 120° for 7 hours, after the temperature had been slowly raised to 120° during

TABLE II.

Examples of mechanism of dimerisation to give ketones of structures in Table I (A = $SnCl_4$).

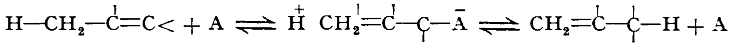


6 hours, but only volatile unsaturated products and unchanged ethyl methylacetoacetate were obtained. After a similar attempt to force the condensation of a very small quantity of *neo*pentyl bromide (kindly supplied by Professor E. D. Hughes of University College, London) with ethyl sodioacetoacetate, hydrolysis of the crude product with concentrated hydrochloric acid at 150° for 7 hours gave much tarry material and no semicarbazone could be obtained from the small amount of steam-volatile product. The structure of the second ketone must, therefore, be left indeterminate for the present. Either of the possible structures (15) or (16 would necessitate an olefin-dimeride structure which could only arise by a fairly deep-seated change in the olefin carbon skeleton during dimerisation. That such extensive rearrangement of carbon skeleton does occur during dimerisation under comparatively mild conditions is well known. It is illustrated, for example, by the results of Brunner and Farmer (*J.*, 1937, 1039) who showed that the bulk of the dimeride formed by the action of boron trifluoride on tetramethylethylene has the structure $CHMe_2{\cdot}CHMe{\cdot}CH{:}CMe{\cdot}CMe_3$ in which the formation of a *tert.*-butyl group is again observed. Incidentally, the proof given in this paper of the structure of one dimeride of trimethylethylene which arises from a " Michael " type of olefin addition may possibly indicate the structure of the unidentified dimeride of tetramethylethylene responsible for the ozonolysis products, acetone and a methyl heptyl ketone, which Brunner and Farmer obtained and regarded as probably derived from a hydrocarbon $C_7H_{15}{\cdot}CMe{:}CMe_2$. A dimeride formed by the " Michael " type addition, *viz.* :



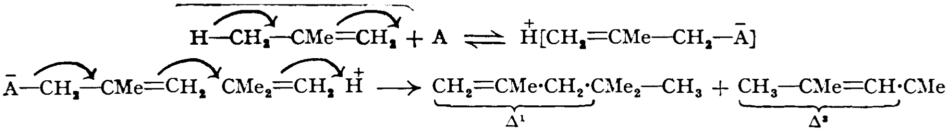
$$H{\cdot}CH_2{\cdot}CMe{:}CMe_2 + BF_3 \rightleftharpoons \overset{+}{H}\ CH_2{:}CMe{\cdot}CMe_2{\cdot}\overset{-}{B}F_3$$
$$\overset{-}{B}F_3{-}CMe_2{-}CMe{=}CH_2\ \ CMe_2{=}CMe\ \ \overset{+}{H} \longrightarrow CMe_2{:}CMe{\cdot}CH_2{\cdot}CMe_2Pr^i \xrightarrow{O_3} COMe_2 + Me{\cdot}CO{\cdot}CH_2{\cdot}CMe_2Pr^i$$

would yield these two products on ozonolysis. If this assumption is correct their unidentified methyl heptyl ketone would be 4 : 4 : 5-trimethyl-*n*-hexan-2-one. A further corollary of the proved ionisation of a proton from an olefin is the possibility of prototropic change both in the parent olefin and in the dimeride :



$$H{-}CH_2{-}C{=}C{<} + A \rightleftharpoons \overset{+}{H}\ CH_2{=}C{-}C{-}\overset{-}{A} \rightleftharpoons CH_2{=}C{-}C{-}H + A$$

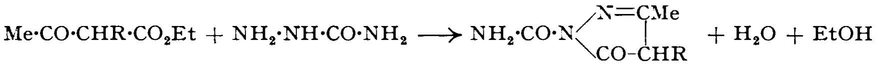
and it is not without significance that such prototropic shift superimposed on an initial addition of the " Michael " type would satisfactorily account for the structures assigned in the literature to the dimerides (formed in acid-catalysed, heterolytic polymerisation) of several simple olefins, *e.g.*, *iso*butene :



$$H{-}CH_2{-}CMe{=}CH_2 + A \rightleftharpoons \overset{+}{H}[CH_2{=}CMe{-}CH_2{-}\overset{-}{A}]$$
$$\overset{-}{A}{-}CH_2{-}CMe{=}CH_2\ \ CMe_2{=}CH_2\ \ \overset{+}{H} \longrightarrow \underbrace{CH_2{=}CMe{\cdot}CH_2{\cdot}CMe_2{-}CH_3}_{\Delta^1} + \underbrace{CH_3{-}CMe{=}CH{\cdot}CMe_3}_{\Delta^2}$$

and both the Δ^1- and Δ^2-isomerides are stated to be formed (McCubbin and Adkins, *J. Amer. Chem. Soc.*, 1930, **52**, 2547). Other examples (including copolymerisations) could be quoted.

In conclusion it has been observed that certain branched-chain alkylacetoacetic esters with semicarbazide acetate do not afford their semicarbazones, but dilution of the reaction mixture after several days precipitates a deep-blue oil which slowly changes into a colourless crystalline material shown to be the corresponding carbamyl-alkylpyrazolone :



$$Me{\cdot}CO{\cdot}CHR{\cdot}CO_2Et + NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2 \longrightarrow NH_2{\cdot}CO{\cdot}N{<}\begin{matrix}N{=}CMe\\ |\\ CO{-}CHR\end{matrix} + H_2O + EtOH$$

These derivatives dissolve, as pseudo-acids, in cold aqueous sodium hydroxide and are reprecipitated unchanged on careful acidification, but boiling with alkali liberates ammonia and then subsequent neutralisation of the excess of alkali with dilute acid precipitates the 3-methyl-4-alkylpyrazolone with liberation of carbon dioxide. Thiele and Strange (*Annalen*, 1894, **283**, 30) observed such pyrazolone formation when the semicarbazone of ethyl acetoacetate was kept in the presence of concentrated ammonia solution for two days at room temperature. The nature of the intermediate deep-blue oil is unknown : it may be due to traces of unrecognised metals present, since Thiele and Strange recorded that the carbamylpyrazolone gives a blue colour with ferric chloride.

Experimental.

(All microanalyses are by Drs. Weiler and Strauss, Oxford. All m. p.s are uncorrected.)

Ozonolysis of the Dimeride of Trimethylethylene.—Repeated fractional distillation either of the polymeride hydrocarbon fraction obtained as a by-product in the trimethylethylene–stannic chloride–phenyl *iso*cyanate reaction (Part II, *loc. cit.*), or of the product of the stannic chloride-induced polymerisation of trimethylethylene alone, gave, eventually, a pure dimeride fraction, b. p. 46°/12 mm. Approx. 4-g. portions of this were dissolved either in pure chloroform or in ligroin (b. p. 40—60°) and ozonised for several days. The solvent was removed in a current of dry air at room temperature and the syrupy ozonide was decomposed by boiling with water under reflux. The volatile products escaping from the top of the condenser were passed into either (1) a solution of 2 : 4-dinitrophenylhydrazine in dilute hydrochloric acid or (2) a solution of *p*-nitrophenylhydrazine in acetic acid. Recrystallisation of the precipitated derivatives from aqueous alcohol gave acetaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 167°, and *p*-nitrophenylhydrazone, m. p. and mixed m. p. 127°. The residual aqueous liquor from the decomposition of the ozonide was extracted with ether, and the ethereal solution was shaken with aqueous sodium carbonate, washed, and dried (Na_2SO_4). Fractional distillation of the residue gave a main ketonic fraction, b. p. 37°/10 mm., together with intermediate (ketonic) fractions, b. p. 38—40°/10 mm. and 42—62°/10 mm., and a small final fraction, b. p. 83—86°/7 mm. (Found : C, 68·9; H, 11·3. $C_9H_{18}O_2$ requires C, 68·4; H, 11·4%), of an unidentified *substance* which gives only a slight turbidity with 2 : 4-dinitrophenylhydrazine and is not a peroxide. The neutralised aqueous residue from the ether-extraction was distilled and the distillate treated with dimedon. It gave only the acetaldehyde–dimedon compound, m. p. and mixed m. p. 141° after crystallisation from alcohol. The sodium carbonate extract, on acidification and ether-extraction, gave only a small amount of liquid with a strong odour of acetic acid. No trace of formaldehyde could be detected in the products of ozonolysis.

Separation of the Semicarbazones of the Ozonolysis Ketones.—The whole ketone fraction was treated with semicarbazide hydrochloride in saturated sodium acetate solution. One crop, S_1, of semicarbazone separated during the first few hours. After its removal, dilution of the reaction mother-liquor gave a second crop S_2. Treatment of S_1 with cold ether and repeated crystallisation of the insoluble portion from 96% alcohol gave the semicarbazone, m. p. 173°, of 4 : 4-dimethyl-*n*-hexane-2-one (II) undepressed by admixture with the semicarbazone of a synthetic specimen of this ketone obtained as described in Part II (*loc. cit.*, p. 731). The 2 : 4-*dinitrophenylhydrazone* had m. p. 78° after crystallisation from 96% alcohol (Found : C, 54·4; H, 6·6; N, 18·0. $C_{14}H_{20}O_4N_4$ requires C, 54·5; H, 6·5; N, 18·2%).

Similar fractional crystallisation of the semicarbazone fraction S_2 from ether gave the *semicarbazone*, m. p. 154°, of an unidentified methyl hexyl ketone (Found : C, 58·2; H, 10·1; N, 22·4. $C_9H_{19}ON_3$ requires C, 58·4; H, 10·3; N, 22·7%). Steam-distillation of this semicarbazone with oxalic acid, saturation of the distillate with salt, and ether-extraction gave the ketone, b. p. 66°/60 mm., which possesses a strong camphoraceous odour and gives a 2 : 4-dinitrophenylhydrazone, m. p. 82° after crystallisation from a very concentrated solution in ether–ligroin (b. p. 40—60°). The ketone gives iodoform with sodium hypochlorite and potassium iodide, but was not obtained in quantity sufficient for a systematic degradation.

Incomplete ozonolysis of the dimeride, b. p. 48—49°/17 mm., from the stannic chloride-catalysed polymerisation of a different sample of trimethylethylene alone gave acetaldehyde and a ketone, the semicarbazone of which gave the material, m. p. 173°, as the only pure product which could be isolated on fractional crystallisation. Re-ozonolysis of the recovered dimeride gave acetaldehyde and the semicarbazone, m. p. 154°, almost uncontaminated with its isomeride. Thus the dimeride of structure (I) would seem to undergo ozonolysis more rapidly than does its isomeride.

Synthesis of Isomeric Methyl Hexyl Ketones.—4 : 5-*Dimethyl*-n-*hexan*-2-*one* (1). The Grignard compound obtained from magnesium (14·4 g.) and *iso*propyl bromide (74 g.) in dry ether (100 c.c.) was refluxed for 30 minutes, and cooled in a freezing mixture (ice-salt). Acetylacetone (28 g., 0·5 mol. proportion) in ether (100 c.c.) was added slowly with mechanical stirring. Towards the end of the addition, separation of a sticky brown mass made stirring difficult. The reaction mixture was refluxed for 15 minutes to help to break up this mass, cooled in a freezing mixture, and decomposed with ice and ammonium chloride. The aqueous liquor was saturated with salt and repeatedly extracted with ether. Fractionation of the residue after removal of the ether (through a Widmer column) from the dried (Na_2SO_4) extract gave two main fractions : (*a*) b. p. 56—60°/11 mm. and (*b*) b. p. 120—125°/12 mm. Analysis of a redistilled specimen, b. p. 60°/11 mm., of (*a*) showed it to be essentially 4 : 5-*dimethyl*-n-*hex*-3-*en*-2-*one* (or its isomeride $CH_2{:}CPr^i{\cdot}CH_2{\cdot}CO{\cdot}CH_3$) (Found : C, 77·1; H, 10·7. $C_8H_{14}O$ requires C, 76·2; H, 11·1%), which affords a *semicarbazone*, m. p. 153° (sinters at 148°) after crystallisation from ether (Found : C, 58·65; H, 9·1. $C_9H_{17}ON_3$ requires C, 59·0; H, 9·3%), and a 2 : 4-*dinitrophenylhydrazone* (red), m. p. 164° after crystallisation from ether containing a trace of ethyl alcohol (Found : C, 54·35; H, 5·8. $C_{14}H_{18}O_4N_4$ requires C, 54·8; H, 5·9%). A (probably) isomeric 2 : 4-*dinitrophenylhydrazone* (orange), m. p. 120° after crystallisation from ligroin (b. p. 40—60°) (Found : C, 55·6; H, 5·6%), was obtained by dilution of the mother-liquor. The unsaturated ketone, b. p. 56—60°/11 mm., was reduced in alcohol with hydrogen and a moderately inactive platinum-black catalyst until saturated, the alcohol from the filtered solution was distilled off through a column, and the residue converted directly into its semicarbazone. Crystallisation from ether gave the 4 : 5-*dimethyl*-n-*hexan*-2-*one semicarbazone*, m. p. 162°, which depressed the m. p. of the semicarbazone of the unsaturated ketone (to 147—150°) and that (m. p. 153°) of the ozonolysis ketone (to 142—146°) (Found : C, 58·6; H, 10·2. $C_9H_{19}ON_3$ requires C, 58·4; H, 10·3%). The corresponding 2 : 4-*dinitrophenylhydrazone* had m. p. 71° after crystallisation from alcohol (Found : C, 53·7; H, 6·3. $C_{14}H_{20}O_4N_4$ requires C, 54·5; H, 6·5%). The red viscous fraction (*b*) is probably the diol, $CH_2(CMePr^i{\cdot}OH)_2$, and was not further examined. If only one molecular proportion of the Grignard reagent is used it merely forms the enolate of the acetylacetone which is recovered unchanged on working up the product.

3 : 3 : 4-*Trimethyl*-n-*pentan*-2-*one* (2). This was prepared essentially by a pinacolic change on

1 : 2 : 3-trimethyl-*n*-pentane-2 : 3-diol (Locquin and Leers, *loc. cit.*) but this diol was obtained by a different route. By use of the combined techniques of Dufraisse and Moureu (*Bull. Soc. chim.*, 1927, [iv], **41**, 855) and Pauly and Leick (*Ber.*, 1900, **33**, 503), mesityl oxide was converted successively into monobromo-, b. p. 70—71°/20 mm. (bromine in ether, followed by the action of piperidine), and acetoxy-, b. p. 74°/12 mm., mesityl oxide (by potassium acetate in absolute alcohol) which was refluxed with 10% sulphuric acid for 2—3 hours to give 4-methyl-*n*-pentane-3 : 4-dione (methyl*iso*propylglyoxal), b. p. 115—116°, as a very volatile, bright yellow liquid, characterised as its *disemicarbazone*, m. p. 223° (decomp.) after crystallisation from boiling alcohol (in which it is not very soluble) (Found : C, 42·3; H, 7·1. $C_8H_{16}O_2N_6$ requires C, 42·1; H, 7·0%), and its *mono-2 : 4-dinitrophenylhydrazone*, m. p. 120° after crystallisation from ether–ligroin (b. p. 40—60°) (Found : C, 48·9; H, 5·1. $C_{12}H_{14}O_5N_4$ requires C, 48·9; H, 4·8%).

The α-diketone (7 g.), dissolved in dry ether (20 c.c.), was added dropwise with constant shaking to the Grignard compound obtained from magnesium (4·8 g.) and methyl iodide (29 g., 2·5 mols.) in ether (60 c.c.) cooled in a freezing mixture. The mixture was well shaken to cause reaction with an orange solid which separated to the top of the reaction mixture, refluxed for 1 hour, and left at room temperature overnight. The mixture was decomposed with ice and ammonium chloride and extracted with ether. After drying (K_2CO_3), the ether was removed through a column and the residue fractionally distilled. Two main fractions, b. p. 69—80°/24 mm. (3 g.) and b. p. 103—106°/23 mm. (3·5 g.), were obtained. The former is probably the *keto-carbinol* $CHMe_2{\cdot}CO{\cdot}CMe_2{\cdot}OH$ which forms a *semicarbazone*, m. p. 196° after crystallisation from alcohol (Found : C, 51·6; H, 9·2; N, 22·6. $C_8H_{17}O_2N_3$ requires C, 51·4; H, 9·1; N, 22·45%). The semicarbazone of the isomeric keto-carbinol $Me{\cdot}CO{\cdot}CMePr^i{\cdot}OH$ is stated (Locquin and Leers, *loc. cit.*) to have m. p. 134°. The higher-boiling fraction is the required diol. This (1·5 g.) was added, with good mechanical stirring, dropwise to concentrated sulphuric acid (12 g.) cooled in a freezing mixture. The mixture was allowed to warm to room temperature and was then poured on crushed ice, and the aqueous liquid was distilled. The ketone, of camphoraceous odour, readily distilled in steam and was obtained by ether-extraction of the first runnings of the distillate. Fractionation of the residue from the dried ethereal solution gave fractions, b. p. 64—75°/59 mm. and 74—78°/56 mm. The former gave the semicarbazone of 3 : 3 : 4-trimethyl-*n*-pentane-2-one (after dilution of the aqueous-alcoholic sodium acetate with water) which, after crystallisation from a concentrated solution in ether–ligroin (b. p. 40—60°), had m. p. 153° in agreement with that recorded by Locquin and Leers (*loc. cit.*). A mixture of this semicarbazone with that, m. p. 154°, of the ozonolysis ketone depressed the m. p. to 139—140°. The crystalline forms of the two semicarbazones, crystallised from the same solvent, are also quite different. The fraction, b. p. 74—78°/56 mm., probably the isomeric ketone $Pr^i{\cdot}CO{\cdot}CMe_3$, was not further investigated.

6-*Methyl*-n-*heptan*-2-*one* (3). *iso*Amyl iodide (14·8 g.) was added to the sodio-derivative of ethyl acetoacetate, prepared from 9·7 g. of the ester and 1·82 g. of sodium in 30 c.c. of absolute alcohol, and the reaction mixture was refluxed for 5·5 hours. Fractional distillation of the product, isolated in the usual manner, afforded, in addition to unchanged materials, ethyl *iso*amylacetoacetate (10 g.), b. p. 127—129°/23 mm. This keto-ester, with semicarbazide hydrochloride in aqueous-alcoholic sodium acetate, exhibited a behaviour which was observed with several branched-chain alkylacetoacetic esters. No precipitation of a semicarbazone occurred during 24—36 hours but dilution then precipitated a deep-blue oil which slowly gave colourless crystals of 1-*carbamyl*-3-*methyl*-4-iso*amylpyrazolone*, m. p. 157° after crystallisation from ether (Found : C, 56·5; H, 7·7; N, 19·3. $C_{10}H_{17}O_2N_3$ requires C, 56·9; H, 8·05; N, 19·9%).

Hydrolysis of ethyl *iso*amylacetoacetate was effected by refluxing with concentrated hydrochloric acid for 3 days. The mixture was diluted and distilled, the distillate was saturated with salt, and the ketone extracted with ether. It was converted directly into its semicarbazone, m. p. 153—155°, after crystallisation from alcohol (lit., m. p. 153°) (Found : C, 58·25; H, 10·1. Calc. for $C_9H_{19}ON_3$: C, 58·4; H, 10·3%). A mixture of this semicarbazone with that, m. p. 154°, of the ozonolysis ketone, had an indefinite m. p., 126—140°. The identity of the synthetic ketone was established by the preparation of its *p*-nitrophenylhydrazone, m. p. 82° (lit., m. p. 83°), and its 2 : 4-*dinitrophenylhydrazone*, m. p. 76° after crystallisation from ether–ligroin (b. p. 40—60°) (Found : C, 54·1; H, 6·3. $C_{14}H_{20}O_4N_4$ requires C, 54·5; H, 6·5%).

3 : 4-*Dimethyl*-n-*hexan*-2-*one* (4). This was prepared by the action of *sec.*-butyl bromide (12·3 g.) on the sodio-derivative obtained from sodium (2·05 g.) and absolute methyl alcohol (30 c.c.) on ethyl methylacetoacetate (11·6 g.). The resulting ethyl methyl-*sec.*-butylacetoacetate, b. p. 107—109°/20 mm., gave no colour with ferric chloride, and was hydrolysed directly with boiling concentrated hydrochloric acid for 24 hours. The product isolated as above contained a large amount of unhydrolysed ester but fractional distillation gave a small amount of a peppermint-smelling ketone, b. p. 65°/13 mm., which gave a *semicarbazone*, m. p. 141° after crystallisation from ether (Found : C, 57·8; H, 10·2. $C_9H_{19}ON_3$ requires C, 58·4; H, 10·3%). The ketone obtained by Powell and Secoy (*loc. cit.*) is described as probably a mixture of isomeric ketones, the semicarbazone of which had m. p. 124—126°. Admixture of the semicarbazone, m. p. 141°, with that, m. p. 154°, of the ozonolysis ketone depressed the m. p. to 124—138°.

3 : 5-*Dimethyl*-n-*hexan*-2-*one* (5). *iso*Butyl bromide (13·7 g.) was refluxed for 6 hours with the potassio-derivative of ethyl acetoacetate, from potassium (3·9 g.) and ethyl acetoacetate (13 g.) in alcohol (50 c.c.). Isolation of the product in the usual manner gave ethyl *iso*butylacetoacetate, b. p. 100—105°/12 mm., which was methylated to give ethyl methyl*iso*butylacetoacetate, b. p. 100—101°/9 mm., characterised as its *semicarbazone*, m. p. 108° after crystallisation from ether–ligroin (b. p. 40—60°) (Found : C, 55·8; H, 8·6. $C_{12}H_{21}O_3N_3$ requires C, 56·4; H, 8·3%). Hydrolysis of this with boiling concentrated hydrochloric acid for 12 hours gave a small yield of the required *ketone*, b. p. 67°/58 mm., of odour similar to, but rather less camphoraceous than, that of the ozonolysis ketone. Its *semicarbazone*, m. p. 115° after crystallisation from ether–ligroin (b. p. 40—60°) (Found : C, 58·0; H, 10·0. $C_9H_{19}ON_3$ requires C, 58·4; H, 10·3%), depresses the m. p. (154°) of the semicarbazone of the ozonolysis

ketone to 103—108°. Its 2 : 4-dinitrophenylhydrazone has m. p. 55° after crystallisation from a very concentrated solution in ligroin (b. p. 40—60°).

5-*Methyl*-n-*heptan*-2-*one* (6). 2-Methyl-*n*-butan-1-ol (" active " amyl alcohol) was converted by the action of phosphorus pentabromide at −5° into the bromide, b. p. 49°/62 mm., 45·3 g. of which were refluxed for 7—8 hours with the sodio-derivative from sodium (6·9 g.) and ethyl acetoacetate (39 g.) in dry ethyl alcohol (100 c.c.). The resulting *ethyl* (2-*methyl*-n-*butyl*)*acetoacetate*, b. p. 114·5°/14 mm., with semicarbazide acetate forms 1-*carbamyl*-3-*methyl*-4-(2-*methyl*-n-*butyl*)*pyrazolone*, m. p. 156° after crystallisation from alcohol and then from ether (Found : C, 56·4; H, 7·7. $C_{10}H_{17}O_2N_3$ requires C, 56·9; H, 8·1%). The structure was confirmed by the following observations. It dissolved in *cold* aqueous sodium hydroxide and was reprecipitated unchanged (m. p. and mixed m. p.) on careful acidification. When it was refluxed with 2N-sodium hydroxide for 1 hour, ammonia was evolved. Acidification of the resulting solution at 0° with dilute hydrochloric acid caused precipitation of a white solid, with evolution of carbon dioxide. The acid was added dropwise until the precipitate just redissolved. Basification with sodium carbonate then precipitated 3-*methyl*-4-(2-*methyl*-n-*butyl*)*pyrazolone*, m. p. 218° after crystallisation from aqueous alcohol (Found : C, 64·1; H, 9·7; N, 16·1. $C_9H_{16}ON_2$ requires C, 64·2; H, 9·6; N, 16·6%).

Prolonged (40 hours) hydrolysis of the acetoacetic ester with boiling concentrated hydrochloric acid gave 5-*methyl*-n-*heptan*-2-*one*, b. p. 91°/55 mm. (Found : C, 74·4; H, 12·1. $C_8H_{16}O$ requires C, 75·0; H, 12·5%), which readily forms a *semicarbazone*, m. p. 138·5° after crystallisation from alcohol (Found : C, 58·2; H, 10·4. $C_9H_{19}ON_3$ requires C, 58·4; H, 10·3%), which depresses the m. p. of the ozonolysis semicarbazone to 110°. The 2 : 4-*dinitrophenylhydrazone*, m. p. 67° (from ether–ligroin) (Found : C, 54·3; H, 6·5. $C_{14}H_{20}O_4N_4$ requires C, 54·5; H, 6·5%), depresses the m. p. (71°) of the corresponding derivative of (1) to 57—63°.

4-*Methyl*-n-*heptan*-2-*one* (7). This ketone was prepared but not characterised by Clarke (*loc. cit.*). *sec.*-Amyl bromide (45·3 g.) was refluxed for 6 hours with the sodio-derivative of ethyl acetoacetate (from 6·9 g. of sodium, and 39 g. of ethyl acetoacetate in 100 c.c. of dry ethyl alcohol) to give *ethyl* sec.-*amylacetoacetate*, b. p. 108°/10 mm. (Found : C, 66·0; H, 10·2. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·0%), which is readily hydrolysed by concentrated hydrochloric acid (24 hours) to give the ketone, b. p. 83°/47 mm. (Found : C, 75·4; H, 12·5. Calc. for $C_9H_{16}O$: C, 75·0; H, 12·5%). The *semicarbazone*, m. p. 108° after crystallisation from ether–ligroin (b. p. 40—60°) (Found : C, 58·1; H, 10·1. $C_9H_{19}ON_3$ requires C, 58·4; H, 10·3%), depresses the m. p. of the ozonolysis semicarbazone to 101° (indefinite). The 2 : 4-dinitrophenylhydrazone has m. p. 54° after crystallisation from ligroin (b. p. 40—60°).

3-*Ethyl*-n-*hexan*-2-*one* (8). This ketone has already been prepared, but not characterised (Clarke and Riegel, *loc. cit.*). Condensation of *n*-propyl bromide with the sodio-derivative of ethyl ethylacetoacetate gave ethyl ethyl-*n*-propylacetoacetate, b. p. 98°/10 mm., which gives no colour with ferric chloride (Found : C, 66·1; H, 10·0. Calc. for $C_{11}H_{20}O_3$: C, 66·0; H, 10·0%). With semicarbazide hydrochloride in saturated sodium acetate no precipitate is formed after several days, but dilution then precipitates an oil which crystallises overnight to yield the true *semicarbazone*, m. p. 104° after crystallisation from ether (Found : C, 56·2; H, 8·7. $C_{12}H_{23}O_3N_3$ requires C, 56·0; H, 9·0%).

Hydrolysis of the acetoacetic ester with boiling 50% sulphuric acid gives the ketone, b. p. 65—68°/56 mm., which slowly affords a *semicarbazone*, m. p. 81° (depressed to 70—80°, by the ozonolysis semicarbazone), after crystallisation from ligroin (b. p. 40—60°) (Found : C, 58·8; H, 10·5. $C_9H_{19}ON_3$ requires C, 58·4; H, 10·3%). The 2 : 4-*dinitrophenylhydrazone*, m. p. 62—64° (Found : C, 54·15; H, 6·35. $C_{14}H_{20}O_4N_4$ requires C, 54·5; H, 6·5%) after crystallisation from a very concentrated solution in ether–ligroin (b. p. 40—60°), also depresses the m. p. of the corresponding derivative of the ozonolysis ketone to 51—55°.

4-*Methyl*-3-*ethyl*-n-*pentan*-2-*one* (9) (Clarke, *loc. cit.*). This substance was similarly obtained from ethyl ethyl*iso*propylacetoacetate, b. p. 96°/10 mm. (Found : C, 65·7; H, 9·7. Calc. for $C_{11}H_{20}O_3$: C, 66·0; H, 10·0%). In agreement with Clarke this ester is extremely difficult to hydrolyse. By prolonged (4—5 days) hydrolysis with boiling aqueous potassium hydroxide a small amount of the ketone was obtained; it was converted directly into its *semicarbazone*, m. p. 121·5° after crystallisation from ligroin (b. p. 40—60°) containing a little ether (Found : C, 58·3; H, 10·2. $C_9H_{19}ON_3$ requires C, 58·4; H, 10·3%), which also depresses the m. p. of the ozonolysis derivative to 105—120°.

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