CCCXXXIII.—*The Chemistry of the Three-carbon System. Part XIX. The Homomesitones.*

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IN searching for readily accessible examples of neutral tautomeric substances, we were led to examine the ketones $C_8H_{14}O$, derived from the intermolecular condensation of methyl ethyl ketone, to which the name homomesitones was applied by Porlezza and Gatti (*Gazzetta*, 1925, **25**, 224). Theoretically, there are four possible homomesitones if the very unlikely formation of the substance $CH_2Me\cdot CMe\vdots CH\cdot CH_2\cdot COMe$ be left out of consideration.

(I.) $CH_2Me\cdot CMe\vdots CH\cdot COEt$ $CHMe\vdots CMe\cdot CH_2\cdot COEt$ (II.)

(III.) $CH_2Me\cdot CMe\vdots CMe\cdot COMe$ $CHMe\vdots CMe\cdot CHMe\cdot COMe$ (IV.)

These two pairs of compounds are related to one another in the same way as the ketones studied by Kon and Linstead (J., 1925, **127**, 815) and should exhibit tautomerism of the same general character. Homomesitones have been obtained by a variety of methods, but little was known of their chemistry until Bodroux and Taboury (*Bull. Soc. chim.*, 1908, **3**, 831; 1909, **5**, 950), who obtained their product with the aid of calcium carbide, attempted to characterise it by means of the very indefinite semicarbazone melting at 119—120°; subsequently, Becker and Thorpe (J., 1922,

121, 1303) obtained the same ketone and concluded that it had the structure (I) because it condensed with ethyl sodiomalonate to a dihydroresorcinol which gave β-methyl-β-ethylglutaric acid on oxidation; a similar conclusion was reached by Ekeley and Howe (*J. Amer. Chem. Soc.*, 1923, **45**, 1917), who prepared their ketone with the aid of both alkaline and acid condensing agents.

The experience accumulated in the last few years suggested that the ketone (II) would probably be encountered together with (I) in the crude homomesitone prepared in the presence of sodium eth‑oxide, whilst the mobility of the three-carbon system present in these compounds would doubtless enable (II) to condense with ethyl sodiomalonate just as readily as (I). Closer investigation brought to light considerable divergences in the properties of homomesitones from different sources, and it was therefore necessary to characterise the different compounds met with. The task proved to be one of great difficulty owing to the extremely intract‑able nature of the mixtures of ketones obtained from methyl ethyl ketone, more especially with the aid of alkaline condensing agents. The semicarbazones prepared from these mixtures are extremely soluble in the crude state, have but little tendency to crystallise, and are probably mixtures of stereoisomerides. For this reason it is only possible to isolate a very small proportion of the constituents of a given mixture in the pure state. We ultimately succeeded in establishing the mutual relationships between the different homo‑mesitones by recourse to synthesis, and the results can be briefly summarised as follows : (*a*) Alkaline condensing agents lead to mixtures of (I) and (II), the former predominating especially in the ketone obtained by Bodroux and Taboury's method; the ketone (I) forms a characteristic *semicarbazone*, m. p. 162°. (*b*) Acid con‑densing agents lead to ketones with a branched chain (III or IV), sulphuric acid giving a ketone of low density, consisting mainly of the βγ-compound (IV), whereas hydrochloric acid yields a ketone of high density and refractive index, consisting mainly of (III); by far the best method is that of Descudé (*Ann. Chim. Phys.*, 1903, **29**, 486), which generally gives (III) only. The formation of ketones with a branched chain is not altogether unexpected, because it has been shown by Harries and his pupils that aromatic aldehydes condense with methyl ethyl and methyl propyl ketones to give compounds such as CHPh:CR·COMe in presence of hydrochloric acid, whilst straight-chain compounds are formed in alkaline solution. It is surprising that Ekeley and Howe did not suspect differences of structure in the homomesitones prepared by them and subse‑quently used for synthetic purposes.

The structure of the homomesitones (I), (III), and (IV) was

confirmed by synthesis from the corresponding acids which were prepared by standard methods; all attempts to synthesise the compound (II), however, were unsuccessful, and the only way in which this substance could be obtained consisted in treating the equilibrium mixture of (I) and (II) with aluminium amalgam which converts (I) into a bimolecular reduction product, leaving the βγ-ketone unattacked.

There are definite indications that the homomesitones are capable of *cis-trans* isomerism ; thus, the ketone (IV) gives two *semicarbazones*, m. p. 203—204° and 163°, although mixtures melting at about 175° are usually encountered. The *semicarbazone* of (III) has a form of m. p. 166—167° in addition to the usual one, m. p. 186°. The ketone obtained by the action of magnesium ethyl iodide on ethyl ethoxycrotonate (Blaise and Maire, *Ann. Chim. Phys.*, 1908, **15**, 566), which forms a semicarbazone (m. p. 158°) *not* identical with that of (I), must be a stereoisomeride of the latter; stereo-isomerism in this case cannot be due to the existence of two forms of the semicarbazone, because the regenerated ketone yields the same semicarbazone on recombining with semicarbazide (compare Locquin and Heilmann, *Compt. rend.*, 1928, **186**, 705). In addition to this, every unsymmetrical ketone can theoretically give rise to two semicarbazones, and it may be that the homomesitones (I) and (II) do actually yield mixtures of *cis-trans* isomeric derivatives, which would in part account for the nature of the semicarbazone usually obtained from them.

Tautomerism of the Homomesitones.—Investigation proves that the homomesitones exhibit tautomerism of the nature to be expected from their structure. In presence of sodium ethoxide or methoxide they form equilibrium mixtures similar to those recently studied by Dickins, Hugh, and Kon (this vol., p. 1630). It is a remarkable fact, however, that both as regards mobility and point of equilibrium the two pairs of homomesitones are very different. Thus, the ketones (I) and (II) form an equilibrium mixture containing 67·5% of the αβ-compound, and this mixture is, as might be expected, indistinguishable from the crude homomesitone obtained by the action of sodium ethoxide on methyl ethyl ketone. The mobility of the system is high, equilibrium being practically established in 24 hours at room temperature. The ketones (III) and (IV) in presence of sodium ethoxide form an equilibrium mixture containing only 17% of the αβ-compound, and the mobility is so low that the equilibration of the αβ-ketone only proceeded half-way in the course of a fortnight at room temperature. The final equilibrium had to be determined at the boiling point of the reagent, and was only reached after 9 hours.

The difference between the two pairs of ketones must evidently be attributed to the effect of the α-methyl group present in (III) and (IV) which has already been found to favour the βγ-phase in some cases (Kon and Narayanan, J., 1927, 1536), although no such effect was observed in the acids studied by Goldberg and Linstead (this vol., p. 2349). The great effect on mobility is certainly unexpected, and further work will be necessary before any explanation is attempted; it is therefore proposed to study several suitable cases in the near future.

EXPERIMENTAL.

Action of Acid Condensing Agents on Methyl Ethyl Ketone.

1. *Sulphuric Acid.*—Ice-cold methyl ethyl ketone was treated with one-tenth of its volume of sulphuric acid, the mixture kept for 24 hours, and worked up as described by Ekeley and Howe (*loc. cit.*). The yield of homomesitones was poor, generally about 10%, b. p. mainly 60—62°/17—19 mm., together with a fraction, b. p. 65—70°. The first fraction, $d_4^{20.8°}$ 0·85845, $n_D^{20.8°}$ 1·44552, was readily converted into a crystalline semicarbazone; this was fractionally crystallised from methyl alcohol, the less soluble portion being obtained in long, transparent laminæ, m. p. about 175°; on repeated crystallisation from ethyl alcohol, the m. p. rose to 203—204°, the compound being identical with the *semicarbazone* of (IV) (see below) (Found : N, 23·3. $C_9H_{17}ON_3$ requires N, 22·9%). The more soluble constituent of the original mixture was obtained in plates, m. p. 134°, evidently consisting of a " eutectic " similar to those previously obtained (compare Kon and Linstead, *loc. cit.*).

The fraction, b. p. 65—70°/17 mm., gave a semicarbazone from which iridescent, anthracene-like plates, m. p. 186°, were obtained on fractional crystallisation from methyl alcohol; these were identical with the semicarbazone of (III) (see below).

A somewhat better yield of homomesitones could be obtained by increasing the amount of condensing agent used; thus from 500 c.c. of methyl ethyl ketone and 200 c.c. of acid in four portions, 82 g., b. p. 53—85°/14 mm., were obtained, from which similar products were isolated.

2. *Hydrochloric Acid.*—The condensation was carried out as described by Ekeley and Howe; in later experiments, the mixture was kept for only 8 days. A yield of some 40% of homomesitone fraction was obtained, boiling mainly above 65°/20 mm.; the principal fraction, b. p. 65—67°/19 mm., had $d_4^{20.4°}$ 0·8689, $n_D^{20.4°}$ 1·45133. The same semicarbazone was obtained from all the fractions; it was purified by grinding with light petroleum, and fractionally crystallised from methyl alcohol. The first crops

usually melted at about 172° and had the characteristic anthracene-like appearance of the αβ-compound, m. p. 186° ; repeated fractional crystallisation from methyl alcohol or acetone raised the m. p. to about 180°, whilst a compound of identical appearance, m. p. 166—167°, was present in the more soluble fraction and was evidently a stereoisomeride. Both semicarbazones gave rise to similar ketones : (a), from the high-melting semicarbazone, b. p. 53°/13 mm., $d_4^{18\cdot8\circ}$ 0·86722, $n_D^{18\cdot8\circ}$ 1·45313, $[R_L]_D$ 39·32 ; (b), from the low-melting semicarbazone, b. p. 53°/13 mm., $d_4^{19\cdot6\circ}$ 0·86567, $n_D^{19\cdot6\circ}$ 1·45233, $[R_L]_D$ 39·32 ; the same semicarbazones were obtainable from these ketones, although the higher-melting compound was clearly not quite homogeneous. This fact and the difficulty in eliminating all traces of halogen from the product caused us to abandon the use of hydrochloric acid as a condensing agent.

3. *Descudé's Method.*—The first experiment according to Descudé's directions (*loc. cit.*) gave a somewhat poor yield of homomesitone which was an inseparable mixture of αβ- and βγ-ketones (III and IV). The following simplified process gave good results : 300 G. of methyl ethyl ketone and 300 g. of acetyl chloride were cooled below 0°, and 120 g. of powdered zinc chloride added, the mixture being kept in the ice-chest for 2 days. Water and a little ether were added, and the oil was washed with sodium carbonate and added to a hot solution of 100 g. potassium hydroxide in 100 c.c. of water and 300 c.c. of alcohol, the mixture being boiled under reflux for 5 minutes. Water was then added, the oil extracted by ether, thoroughly washed, dried, and fractionated with a good column. The fractions obtained were : (a) up to 50°/20 mm., 30 g. ; (b) 50—55°/18 mm., 9 g. ; (c) 55—58°/17 mm., 22 g. ; (d) 58—63°/16 mm., 27 g. ; (e) 63—73°/15 mm., 38 g. Fractions (b), (c), and (d) were converted into the *semicarbazone* which formed characteristic plates, m. p. 186° after one crystallisation, and was identical with the synthetic specimen (see below) (Found : C, 59·0 ; H, 9·4. $C_9H_{17}ON_3$ requires C, 59·0 ; H, 9·4%). The ketone regenerated from it with oxalic acid had b. p. 53°/10 mm., 160°/750 mm., $d_4^{19\cdot5\circ}$ 0·86957, $n_D^{19\cdot5\circ}$ 1·45293, $[R_L]_D$ 39·19 ; it had a strong, pleasant odour. The fraction (a) consisted of methyl ethyl ketone and some of the βγ-ketone which could be isolated in the form of its semi-carbazone. The fraction (e) still contained chlorine and was there fore again treated with alkali, whereby a mixture of the two homo-mesitones was obtained, the αβ- predominating. A greater pro-portion of the βγ-ketone was obtained on more prolonged treatment with alkali ; thus, after 3 hours' boiling with sodium ethoxide in excess, it became the main product.

Synthesis of Ketone (III).—Methyl ethyl ketone was condensed

with ethyl α-bromopropionate in the presence of zinc to *ethyl β-hydroxy-αβ-dimethyl-n-valerate*, b. p. 89—90°/13 mm., $d_4^{19.5°}$ 0·96457, $n_D^{19.5°}$ 1·4319 (75% yield). The acid obtained by alkaline hydrolysis was liquid. It was dehydrated by boiling with acetic anhydride and gave a poor yield of *αβ-dimethyl-Δ^α-pentenoic acid*, b. p. 116°/18 mm., $d_4^{17.5°}$ 0·97497, $n_D^{17.5°}$ 1·45952, $[R_L]_D$ 36·06 (calc., 35·60). The *acid chloride* boiled at 66°/17 mm., and gave a p-*toluidide* forming long needles, m. p. 123° (Found : C, 77·3 ; H, 8·7. $C_{14}H_{19}ON$ requires C, 77·4 ; H, 8·8%). The acid chloride was treated with zinc methyl iodide (compare Dickins, Hugh, and Kon, *loc. cit.*), giving a moderate yield of ketone which was converted into the semicarbazone and the latter recrystallised from methyl alcohol. The first crop separated in characteristic anthracene-like crystals, m. p. 180—182°, identical with the semicarbazone prepared by the Descudé method. Subsequent crops melted much lower and were evidently impure. The ketone, *γδ-dimethyl-Δ^γ-hexen-β-one* (III), regenerated from the first crop of semicarbazone had b. p. 65°/20 mm., $d_4^{17.4°}$ 0·86856, $n_D^{17.4°}$ 1·45283, $[R_L]_D$ 39·23, and was in every way identical with that obtained by Descudé's method.

Synthesis of Ketone (IV).—Ethyl β-hydroxy-αβ-dimethyl-*n*-valerate was readily dehydrated with phosphorus oxychloride in benzene, giving a 95% yield of *ethyl αβ-dimethyl-Δ^β-pentenoate*, b. p. 69°/13 mm., $d_4^{21.1°}$ 0·92379, $n_D^{21.1°}$ 1·43628. The *acid*, obtained by allowing the ester (1 g.-mol.) to stand at room temperature with 70 g. of sodium hydroxide in 700 c.c. of aqueous alcohol for 3 days (compare Linstead and May, J., 1927, 2565), had b. p. 116°/20 mm., $d_4^{18.2°}$ 0·97002, $n_D^{18.2°}$ 1·4498, $[R_L]_D$ 35·50 (calc., 35·60). The *acid chloride* boiled at 52°/13 mm., and gave a p-*toluidide* which had little tendency to crystallise but formed needles, m. p. 56°, from dilute alcohol (Found : C, 77·5 ; H, 8·7. $C_{14}H_{19}ON$ requires C, 77·4 ; H, 8·8%). The acid chloride gave on treatment with zinc methyl iodide a 50—60% yield of ketone, but an 85% yield was more readily obtained by slowly adding magnesium methyl iodide to a well-cooled ethereal solution of the acid chloride. The ketone was isolated in the form of its sparingly soluble semicarbazone ; this separated very rapidly, and after one crystallisation melted at about 175°, rising to 203—204° after repeated crystallisation. The regenerated ketone, *γδ-dimethyl-Δ^δ-hexen-β-one* (IV), had a characteristic camphoraceous odour, b. p. 48°/12 mm., 154°/750 mm., $d_4^{19.2°}$ 0·85385, $n_D^{19.2°}$ 1·43768, $[R_L]_D$ 38·74 (calc., 38·72). It was found that another *semicarbazone* was generally present and sometimes constituted the sole product; this had a very similar appearance (long, flattened needles) but melted at 163°, and the ketone regenerated from it was indistinguishable from the above,

b. p. $45°/10$ mm., $d_{4°}^{16·9°}$ $0·85601$, $n_D^{16·9°}$ $1·4401$, but gave the low-melting semicarbazone on treatment with semicarbazide. This ketone was frequently obtained as the main product on treating the intermediate fractions of the " Descudé ketone " with hot sodium ethoxide.

Equilibrium between Ketones (III) and (IV).—For the analysis of mixtures of the two ketones, the method of Linstead and May (*loc. cit.*) was used. The values obtained in 10 minutes with $M/300$-solutions in chloroform were

Mixture (% $\alpha\beta$)	0	10	25	50	75	90	100
% Iodine addition	81·8	77·7	69·6	50·6	28·4	14·5	3·4

from which a reference curve was constructed.

1. *Point of equilibrium.* Equilibrium was only slowly established at room temperature. Samples of the two pure ketones were therefore treated with a slight excess of sodium in methyl alcohol (4% solution) and warmed on the steam-bath under reflux for 6 hours; the ketones were then isolated as described by Dickins, Hugh, and Kon (*loc. cit.*), analysed iodometrically, and again treated with the reagent.

Initial material :	$\alpha\beta$-Ketone.			$\beta\gamma$-Ketone.	
Time (hours)	6	12	18	6	12
% Iodine addition	58·9	73·5	73·8	74·5	74·3
% $\alpha\beta$-Ketone	40·0	18·25	17·25	16·5	16·75

The equilibrium point is therefore $17 \pm 0·25\%$.

2. *Mobility.* The first experiments were carried out by adding a cold solution of sodium (4 g.) in 75 c.c. of methyl alcohol to 18·3 g. of the ketone, making the volume up to 100 c.c. with methyl alcohol, and keeping the mixture at room temperature, 20 c.c. of solution being withdrawn at intervals for analysis.

Initial material :		$\alpha\beta$-Ketone.					
Time (hours)	24	48	72	96·5	121	235	422
% Iodine addition ...	11·7	16·6	18·4	22·4	27·0	37·9	46·2
% $\alpha\beta$-Ketone	92·5	87·5	85·5	81·05	76·5	64·75	55·5

Initial material :	$\beta\gamma$-Ketone.		
Time (hours)	96	165	306
% Iodine addition ...	79·5	78·9	78·1
% $\alpha\beta$-Ketone	5·75	6·75	9·0

The values for 235 and 422 hours were obtained by combining the five fractions of ketone isolated, taking them as corresponding to 72 hours, and again treating them with sodium methoxide. Only a few experiments were performed with the $\beta\gamma$-ketone, because this was apt to give erratic results. Finally, in order to obtain an estimate of mobility comparable with that of the ketones (I) and

(II) (see below), the αβ-ketone was treated with N-sodium methoxide (1 equiv.) at 25° :

Time (hours)	24	48	72
% Iodine addition	14·6	17·2	20·9
% αβ-Ketone	89·5	86·5	82·5

The change thus proceeded somewhat more quickly at 25°, although the total concentration of the reactants was lower.

Action of Alkaline Condensing Agents on Methyl Ethyl Ketone.

1. *Calcium Carbide.*—The condensation was carried out essentially as described by Bodroux and Taboury (*loc. cit.*); the yield of homomesitone fraction varied, the best being about 55%. On redistillation, the bulk of the product boiled at 67—70°/20 mm. and had $d_4^{22\cdot8°}$ 0·85523, $n_D^{22\cdot8°}$ 1·44973, $[R_L]_D$ 39·57; these properties indicate a high percentage of αβ-ketone, but this varies in different preparations. The semicarbazone was prepared in the usual way and proved to be an extremely intractable material from which only a minute proportion of pure substances could be isolated. Washing with light petroleum and fractional crystallisation from methyl alcohol led to the isolation of a very small amount of a less soluble constituent (in addition to the completely insoluble disemicarbazone already obtained by Ekeley and Howe, *loc. cit.*). This separated in pearly plates, m. p. 162°, and was the *semicarbazone* of the ketone (I) (see below) (Found : N, 23·1. $C_9H_{17}ON_3$ requires N, 22·9%). From the more soluble portions, less definite solids of varying m. p. were obtained, mainly the " eutectic " melting at 123°; this gave a ketone very similar in properties to the pure αβ-ketone, *viz.*, b. p. 50—52°/9 mm., $d_4^{18\cdot8°}$ 0·85731, $n_D^{18\cdot8°}$ 1·45193, $[R_L]_D$ 39·64. On one occasion a very small amount of needles, m. p. 156°, was isolated, which depressed the m. p.'s of all the other pure semicarbazones, but the amount was insufficient for investigation. On another occasion a preparation, m. p. 137°, was isolated which appeared to be a definite compound, and the ketone regenerated from it had b. p. 52—53°/12 mm., $d_4^{19\cdot8°}$ 0·85777, $n_D^{19\cdot8°}$ 1·45163, $[R_L]_D$ 39·63. On recombination with semicarbazide, a mixture was obtained from which a small amount of the compound of m. p. 162° could be isolated.

2. *Sodium Ethoxide.*—The following simplified preparation gave satisfactory results : Sodium (60 g.) was dissolved in ethyl alcohol (900 c.c.) and the excess of alcohol evaporated off under reduced pressure at about 80° ; to the mixture, cooled in ice and salt, 500 c.c. of methyl ethyl ketone were added and the whole was kept for 24 hours with occasional shaking. Water was then added, the oil taken up in ether, well washed, dried, and distilled, the yield

of homomesitone fraction (b. p. 62—70°/19 mm.) being 90—100 g. The main bulk had $d_4^{21\cdot4^\circ}$ 0·85656, $n_D^{21\cdot4^\circ}$ 1·44502, iodine addition 34·3%. A specimen of the ketone prepared by the carbide process gave, on treatment with excess of sodium ethoxide, a product of very similar properties and iodine addition, which are characteristic of the equilibrium mixture of αβ- and βγ-ketone.

The semicarbazone of this equilibrium mixture was prepared, but it was again found impossible to isolate more than a small amount of pure material from it, although the αβ-semicarbazone, m.p. 162°, was obtained without great difficulty.

Synthesis of the Ketone (*I*).—β-Methyl-β-ethylacrylic acid was prepared as described by Kon and Linstead (J., 1925, **127**, 616) or by Fichter, Kieffer, and Bernoulli's method (*Ber.*, 1909, **42**, 4710). The acid chloride was then added to zinc ethyl iodide, and the moderate yield of ketonic fraction obtained was converted into the semicarbazone, which crystallised from methyl alcohol in anthracene-like plates, m. p. 162°, identical with the compound isolated from homomesitone (Found : C, 59·2; H, 9·3. Calc. for $C_9H_{17}ON_3$: C, 59·0; H, 9·3%). The regenerated ketone, *ε-methyl-Δ⁸-hepten-γ-one*, had b. p. 66°/18 mm., 53—54°/8 mm., $d_4^{21\cdot5^\circ}$ 0·85516, $n_D^{21\cdot5^\circ}$ 1·45073, $[R_L]_D$ 39·69 (calc., 38·72); its odour was strong and not very pleasant.

Isolation of Ketone (*II*).—Numerous attempts to obtain this ketone from β-methyl-Δᵝ-pentenoic acid (Kon and Linstead, *loc. cit.*) by the action of zinc ethyl iodide on the chloride or of magnesium ethyl iodide on the amide were fruitless, although in the latter case a small amount of liquid with a ketonic smell was obtained but could not be purified. The chloride of the acid* was allowed to react with ethyl sodiomethylacetoacetate in ethereal solution, a good yield of the new ester, $CHMe\mathord{:}CMe\cdot CH_2\cdot CO\cdot CMe(CO_2Et)\cdot COMe$, b. p. 158—168°/19 mm., being obtained; this was hydrolysed by boiling with 10% alcoholic sodium hydroxide for ½ hour, and the ketone formed isolated by distillation in steam : b. p. 74—76°/27 mm., $d_4^{20\cdot4^\circ}$ 0·85595, $n_D^{20\cdot4^\circ}$ 1·4453, $[R_L]_D$ 39·24. The semicarbazone was crystallised from methyl alcohol, and the resulting plates, m. p. 162°, were identified as the αβ-compound, showing that equilibration of the ketone had taken place during hydrolysis.

The ketone was finally isolated by treating the equilibrium mixture from the sodium ethoxide condensation with aluminium

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* It should be noted that the acid prepared by the action of sulphuric acid on the hydroxy-acid (*loc. cit.*) contains some αβ-acid. The purest acid is obtained by the cold hydrolysis of the ester obtained by dehydrating the hydroxy-ester with phosphorus oxychloride or potassium hydrogen sulphate. The use of phosphorus pentoxide leads to a mixture of esters.

amalgam (Harries and Eschenbach, *Ber.*, 1896, **29**, 380), whereby the αβ-ketone was reduced to a high-boiling bimolecular condensation product; the unchanged βγ-ketone was then isolated by careful fractionation. The reduction was carried out twice to ensure the complete removal of the αβ-ketone, although the iodine addition of the product did not change. The new compound, ε-*methyl*-Δ^ε-*hepten*-γ-*one*, thus obtained had b. p. 63°/19 mm., $d_4^{21\cdot2°}$ 0·85244, $n_D^{21\cdot2°}$ 1·43668, $[R_L]_D$ 38·73 (calc., 38·72); the odour of the ketone was more pleasant than that of the αβ-ketone and quite distinctive. Several different preparations had very similar properties and no saturated ketone, $C_8H_{16}O$, appeared to be produced in the reduction. The *semicarbazone*, although readily formed, was soluble and difficult to purify; it separated from methyl alcohol or ethyl acetate in indefinitely crystalline nodules, m. p. 134° (Found : N, 23·2. $C_9H_{17}ON_3$ requires N, 22·9%).

Equilibrium between the Ketones (I) and (II).—Mixtures of the two ketones were analysed iodometrically with the aid of a reference curve, constructed from the following figures :

Mixture (% αβ-)	0	10	25	50	75	90	100
% Iodine addition	75·3	71·6	64·2	48·7	29·4	16·2	7·8

the αβ-ketone used being regenerated from the pure semicarbazone; the βγ-ketone was the specimen described above.

1. *Point of equilibrium.* The βγ-ketone was treated with hot sodium methoxide for 6 hours and gave a product, $d_4^{20\cdot2°}$ 0·85898, $n_D^{20\cdot2}$ 1·4442, iodine addition 38·8%; on further treatment the value dropped to 35·4 and then remained constant. The ketone prepared by the method of Bodroux and Taboury and purified by regeneration from the semicarbazone was similarly treated and found to have the same iodine addition (35·3%). The composition of this mixture is 67·5% αβ-ketone. This incidentally proved that the βγ-ketone used was free from saturated impurities, otherwise a lower % addition of iodine would have been observed on complete equilibration.

2. *Mobility.* An exactly N-solution of sodium in methyl alcohol was added to each of the ketones in molecular proportion; the two mixtures were kept in a thermostat at 25°, and portions withdrawn at intervals for analysis gave the following result :

Initial material : αβ-Ketone.

Time (hours)	1	2	3	5	7	28	72
% Iodine addition	21·80	24·49	26·35	29·10	27·47	32·20	35·05
% αβ-Ketone	84·0	80·75	78·75	77·75	77·25	72·00	67·75

Initial material : βγ-Ketone.

Time (hours)	1	2	4	6	8	28
% Iodine addition	59·95	53·05	45·10	41·30	39·10	35·80
% αβ-Ketone	32·50	44·00	55·00	60·25	63·00	67·00

Ketone, $C_8H_{14}O$, *from Ethyl Ethoxycrotonate and Magnesium Ethyl Iodide*.—Blaise and Maire's preparation (*loc. cit.*) was repeated. The ketonic fraction (obtained in extremely poor yield) was treated with semicarbazide, and the resulting semicarbazone crystallised in small plates which did not felt together; it melted at 158° after several crystallisations from methyl alcohol and was not identical with any of the semicarbazones isolated in the course of this work. The ketone regenerated from it differed from the ketone (I) in smell, although its properties were otherwise very similar : b. p. 49°/8 mm., $d_4^{15 \cdot 8°}$ 0·86004, $n_D^{15 \cdot 8°}$ 1·45233, $[R_L]_D$ 39·58; it gave the same semicarbazone on recombining with semicarbazide. The high molecular refraction and low iodine value indicate an $\alpha\beta$-structure, but the quantity at our disposal did not allow of more thorough investigation.