481. *The Rearrangement of Ketones containing Tertiary Alkyl Groups.*

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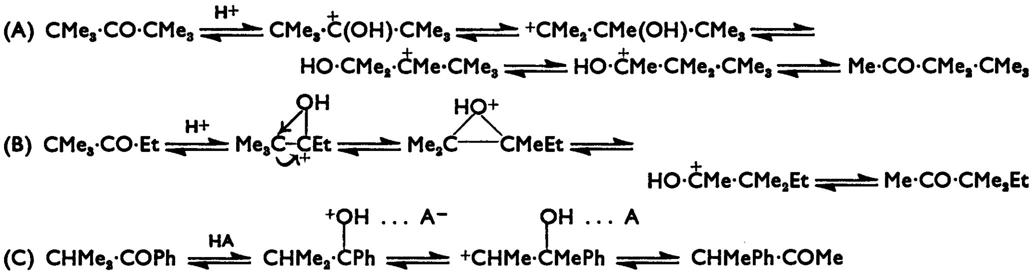
Ketones in which the carbonyl group is attached to two *tert.*-alkyl groups, or one *tert.*- and one *sec.*-alkyl group, rearrange under the influence of sulphuric acid to ketones containing a primary alkyl group. The use of labelled carbon shows that migration of the oxygen atom is not involved in the reaction.

The formation of 3 : 3 : 4 : 4-tetramethylpentan-2-one by the action of sulphuric acid on di-*tert.*-butyl ketone[1] suggested the use of this reaction as a convenient means for the synthesis of compounds containing contiguous quaternary carbon atoms.

The effect of concentrated sulphuric acid on *tert.*-butyl 1 : 1-dimethylpropyl, *tert.*-butyl *iso*propyl, *tert.*-butyl *neo*pentyl, *tert.*-butyl ethyl, di*iso*propyl, and di*iso*butyl ketone was therefore investigated. Only in the first two cases were good yields of rearrangement products (4 : 4 : 5 : 5-tetramethylhexan-3-one and 3 : 3 : 4-trimethylpentan-2-one) obtained. More than 90% of the original ketone was recovered in each of the other cases. These results suggest that, for rearrangement to take place, it is necessary for the carbonyl group to be attached to two quaternary carbon atoms or one quaternary and one ternary carbon. Favorski[2] showed that *tert.*-butyl phenyl ketone was converted into 3-methyl-3-phenylbutan-2-one by heating it with zinc chloride, and a number of workers[3] have investigated the rearrangement of ketones in which the carbonyl group is attached directly to an aromatic group. They also found that it is necessary for the carbonyl group to be attached to a quaternary or ternary carbon atom. Aldehydes in which the carbonyl group was attached to a ternary carbon were also rearranged to ketones.

Zook and Paviak[4] report a 9% conversion of *tert.*-butyl ethyl ketone into 2 : 2-dimethylpropyl methyl ketone, identifying the product by means of infrared spectrometry. In the present work no attempt has been made to search for small amounts of rearranged products.

Three mechanisms for the rearrangement have been suggested. Mechanisms A (Barton, Morton, and Porter[1]) and B (Zook and Paviak[4]) involve the migration of the oxygen atom. In mechanism C (Zalesskaya[5]) the oxygen remains attached to its carbon atom. The two types could thus be identified by use of labelled carbon. Di-*tert.*-butyl [^{14}C]ketone was treated with sulphuric acid, and the rearranged ketone was oxidised to ααββ-tetramethylbutyric acid, the silver salt of which with bromine or iodine gave radioactive carbon dioxide. A mechanism of the type proposed by Zalesskaya must therefore be correct.



$$\text{(A)}\ \mathrm{CMe_3{\cdot}CO{\cdot}CMe_3} \overset{H^+}{\rightleftharpoons} \mathrm{CMe_3{\cdot}\overset{+}{C}(OH){\cdot}CMe_3} \rightleftharpoons \mathrm{{}^+CMe_2{\cdot}CMe(OH){\cdot}CMe_3} \rightleftharpoons \mathrm{HO{\cdot}CMe_2{\cdot}\overset{+}{C}Me{\cdot}CMe_3} \rightleftharpoons \mathrm{HO{\cdot}\overset{+}{C}Me{\cdot}CMe_2{\cdot}CMe_3} \rightleftharpoons \mathrm{Me{\cdot}CO{\cdot}CMe_2{\cdot}CMe_3}$$

$$\text{(C)}\ \mathrm{CHMe_2{\cdot}COPh} \overset{HA}{\rightleftharpoons} \mathrm{CHMe_2{\cdot}\overset{{}^+OH\,\ldots\,A^-}{C}Ph} \rightleftharpoons \mathrm{{}^+CHMe{\cdot}\overset{OH\,\ldots\,A}{C}MePh} \rightleftharpoons \mathrm{CHMePh{\cdot}COMe}$$

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[1] Barton, Morton, and Porter, *Nature*, 1952, **169**, 373.
[2] Favorski, *Bull. Soc. chim. France*, 1936, **3**, 239.
[3] Danilov, Danilova, Tiffeneau, and others; see Zalesskaya, *Zhur. obshchei Khim.*, 1948, **18**, 1172, for a bibliography.
[4] Zook and Paviak, *J. Amer. Chem. Soc.*, 1955, **77**, 2501.
[5] Zalesskaya, *Zhur. obshchei Khim.*, 1948, **18**, 1168.

The ketones rearrange equally in the presence or absence of an inert solvent, although a small amount of decomposition takes place in its absence. When benzene is present, no toluene or butylbenzene is formed; so the methyl and the *tert.*-butyl group are presumably never completely separated from the rest of the molecule. Each of the three suggested mechanisms, however, postulates the intermediate formation of one or more large carbonium ions, but no evidence was found of the formation of tetramethylphenylpentanol. This may be due to the large size of the ion and the fact that it contains oxygen.

The silver salt of tetramethylbutyric acid does not react normally with halogens. Two mols. of the salt are required to react with one of halogen, and this normally gives rise to an ester: $2R{\cdot}CO_2Ag + I_2 = R{\cdot}CO_2R + CO_2 + 2AgI$. In the present instance, the identifiable products are one mol. each of the free acid and carbon dioxide, and two of silver iodide, even when excess of bromine or iodine is used. This may be due to the difficulty of forming this ester or to its rapid hydrolysis by water; attempts to synthesise it by the usual methods were unsuccessful.

EXPERIMENTAL

Rearrangement of Ketones.—Except where otherwise specified, the ketones were shaken or stirred for 24 hr. with 7 vols. of benzene and 5 vols. of concentrated sulphuric acid. The mixture was poured on crushed ice, the aqueous layer extracted with benzene, and the benzene solution was dried and fractionally distilled.

(*a*) Di-*tert.*-butyl ketone, b. p. 152°, n_D^{20} 1·4193, gave 85% of its weight of 3 : 3 : 4 : 4-tetramethylpentan-2-one, b. p. 165·5—166·5°, m. p. 55°, identified by its semicarbazone, m. p. and mixed m. p. 204°, and by oxidation with 50% nitric acid to 1 : 1 : 2 : 2-tetramethylbutyric acid, m. p. and mixed m. p. 196°. No toluene or *tert.*-butylbenzene was found. When toluene was used as a diluent, no other benzene derivatives were found in the product. When no organic solvent was used, the yield of rearranged ketone was somewhat less (75%).

(*b*) *tert.*-Butyl 2 : 2-dimethylpropyl ketone, b. p. 174·5—175·5°, n_D^{20} 1·4293, on treatment as above gave a fraction, b. p. 182°, n_D^{20} 1·4451. This gave no semicarbazone or dinitrophenylhydrazone, but was identified as 2 : 2 : 3 : 3-*tetramethylhexan*-4-*one* by analysis (Found: C, 76·75; H, 13·15. $C_{10}H_{20}O$ requires C, 76·85; H, 12·95%), and by oxidation to tetramethylbutyric acid with 50% nitric acid.

(*c*) *tert.*-Butyl *iso*propyl ketone gave an 80% yield of 2 : 3 : 3-trimethylpentan-4-one, b. p. 150—152°, n_D^{20} 1·4161, identified as semicarbazone, m. p. 150—151°, and by oxidation to ααβ-trimethylbutyric acid, m. p. 53°.

(*d*) *tert.*-Butyl *neo*pentyl ketone, *tert.*-butyl ethyl ketone, di*iso*propyl ketone, and di*iso*butyl ketone gave 85%, 90%, 97% and 90% yields respectively of unchanged ketone.

*Rearrangement of Di-*tert.*-butyl Ketone containing* ^{14}C.—(a) *Preparation.* The carbon dioxide from barium carbonate (15 g.) containing 0·25 mc of ^{14}C was passed into 1·46M-ethereal *tert.*-butylmagnesium chloride (70 ml., 1·35 mols.). The crude αα-dimethylpropionic acid obtained in the usual way (7·5 g.; m. p. 15—20°) was mixed with benzoyl chloride (24 g., 1·15 mols.) and gradually heated to 180° during 3 hr. The chloride was obtained on distillation *in vacuo* (7·5 g., 85%). *tert.*-Butylmagnesium chloride (75 ml.; 1·46M) was added dropwise to the acid chloride and anhydrous cuprous chloride (7 g.) in anhydrous ether. After refluxing, the mixture was poured on ice, and the crude ketone (7·9 g., 75% based on $BaCO_3$) was separated.

(b) *Rearrangement.* The crude ketone was shaken for 24 hr. with concentrated sulphuric acid (50 ml.) and benzene (75 ml.). The mixture was poured on ice, and the rearranged ketone (8 g.) was isolated. On distillation the main bulk came over at 163—167°.

(c) *Oxidation.* The rearranged ketone (1·1 g.) was oxidised by refluxing 50% nitric acid (40 ml.). After addition of water, the organic acid was extracted with ether. After one recrystallisation, the ααββ-tetramethylbutyric acid melted at 192—194°.

(d) *Decarboxylation.* Iodine (0·26 g., 1·04 mol.) in dry benzene was added to the dry silver salt (0·5 g.) prepared from the above acid. No reaction occurred in the cold, but on warming nearly to the b. p. the colour was gradually discharged; the carbon dioxide evolved was carried by a slow stream of dry nitrogen into barium hydroxide solution. The barium carbonate (0·155 g., 80%) was filtered off and washed under conditions which excluded contamination by atmospheric carbon dioxide. The benzene solution was slightly coloured with iodine, and after separation of silver iodide, the colour was removed by shaking with 0·3 ml. of 0·5N-thiosulphate. The organic acid (0·152 g., 106%) was extracted from the benzene layer with aqueous sodium hydroxide, and isolated by acidification with mineral acid. The residual benzene solution on distillation, left only a very small amount of gum.

The high yield of recovered acid and low yield of barium carbonate appear to be due to the difficulty of completely excluding water under the conditions of experiment. In some experiments in which insufficient precautions were taken, as much as 125% of recovered acid and a proportionately low yield of barium carbonate were obtained. In each case the yield of barium carbonate, based on the amount of acid not recovered, was about 80—85%.

The acid from which the silver salt was prepared gave counts of 1380 and 1349 per min. with a Geiger–Müller counter. Under similar conditions the recovered acid gave counts of 1334, 1291, and 1355, and the barium carbonate 1208 and 1124.

Attempts to prepare the 2 : 2 : 3-*Trimethylbutyl Ester of* αα\ββ-*Tetramethylbutyric Acid*.—(*a*) Equivalent amounts of the alcohol, acid, and trifluoroacetic anhydride were left at 60° for 6 hr. When the volatile products were removed in a vacuum-desiccator, the residue consisted of unchanged acid. Alternatively, the reaction product was separated into unchanged acid and alcohol by extraction of its chloroform solution with aqueous sodium hydrogen carbonate.

(*b*) Refluxing the silver salt of the tetramethylbutyric acid with 2-chloro-2 : 3 : 3-trimethylbutane in ether did not afford silver chloride. After several hours a small amount of black precipitate was formed.

(*c*) 2 : 3 : 3-Trimethylbutan-2-ol was shaken in dry ether with sodium till reaction ceased. The undissolved sodium was removed and the mixture refluxed with the acid chloride prepared from tetramethylbutyric acid and thionyl chloride. No reaction appeared to take place, and unchanged acid and alcohol were recovered.

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