3. The reliability of the method of analysis using measurements of the freezing point which are employed in this and in our preceding investigation, has been confirmed by measurements made by two other independent methods.

WORCESTER, MASS. RECEIVED MARCH 16, 1943

[CONTRIBUTION OF THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

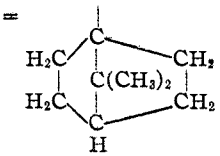
Reactions of Atoms and Free Radicals in Solution. V. The Non-coplanar Free 1-Apocamphyl Radical

BY M. S. KHARASCH, FRANCES ENGELMANN AND W. H. URRY

All free radicals of type $R_1R_2R_3C\cdot$ which have hitherto been described, whether they be of long half-life period (expressed in years) or of short half-life period (expressed in thousandths of a second), yield optically inactive products of the form $R_1R_2R_3CX$. Presumably this optical inactivity is due to the ability of the free radical to assume a coplanar configuration in at least one phase of its internal vibrations. Note, for instance, the optical inactivity of the 1,2-dichloro-2-methylbutane prepared by the chlorination of 1-chloro-2-methylbutane,[1] a reaction in which the free radical $(CH_3)(C_2H_5)\dot{C}CH_2Cl$ is an intermediate. It is, however, possible to prepare free radicals which cannot assume a coplanar configuration. Since the behavior of such free radicals in solution is of considerable theoretical interest, an investigation of the methods of preparing a number of these substances has been undertaken. The present paper contains evidence for the existence of the non-coplanar free 1-apocamphyl radical. Other radicals of this type will be reported in a future publication, and the theoretical significance of the findings will there be discussed.

Preparation and the Reactions of the Free 1-Apocamphyl Radical.—The free 1-apocamphyl radical was generated in carbon tetrachloride solution by heating the peroxide of apocamphane-1-carboxylic acid. The following products, in the quantities indicated, were isolated.[2]

R = 1-apocamphyl radical =



$$(RCOO—)_2 \xrightarrow{CCl_4} \underset{(36\%)}{RCl} + \underset{(9\%)}{RR} + \underset{(50\%)}{RCOOR} + \underset{(5\%)}{RCOOH} + C_2Cl_6$$

The peroxide of apocamphane-1-carboxylic acid is unusually stable; it is completely decomposed only after being heated for about twenty hours in the carbon tetrachloride solution. The separation of the solvent and of the various reaction products was quite difficult. A vacuum technique had to be developed to separate the carbon tetrachloride from 1-chloroapocamphane and hexachloroethane, both of which are extremely volatile. These last two substances could not be separated by physical means, but it was found possible to destroy the hexachloroethane without breaking down the 1-chloroapocamphene, since the latter compound[3] is not readily attacked by inorganic bases. However, in spite of the difficulties mentioned, the course of the reaction was most satisfactory; no tar was formed, and it was possible to account quantitatively for all the peroxide used (see above).

The formation of all the products found is probably best accounted for by the mechanism

R· = 1-apocamphyl radical

(1) $RCOO—OOCR \longrightarrow R\cdot + CO_2 + RCOO\cdot$
(2) $R\cdot + CCl_4 \longrightarrow RCl + Cl_3C\cdot$
(3) $R\cdot + RCOO\cdot \longrightarrow RCOOR$
(4) $R\cdot + RCOO—OOCR \longrightarrow RCOOR + RCOO\cdot$
(5) $R\cdot + R\cdot \longrightarrow RR$
(6) $R\cdot + RCOO—OOCR \longrightarrow RR + CO_2 + RCOO\cdot$
(7) $RCOO\cdot \longrightarrow R\cdot + CO_2$
(8) $Cl_3C\cdot + \cdot CCl_3 \longrightarrow C_2Cl_6$

In view of the high stability of the peroxide and the consequent low concentration of the free radical R· at any one moment, formation of the ester and the dimer (bi-1-apocamphyl), according to reactions (4) and (6), seems to us more probable than their formation according to reactions (3) and (5).[4]

The type of decomposition given above is characteristic only for stable organic peroxides. Since the concentration of free radical resulting from the decomposition of such peroxides is at no time large, and since, in the experiments described, the yield of ester is about the same as the yield of chloro compound, the energy of activation required to remove a chlorine atom from carbon tetrachloride (reaction (2)) is probably about the same as that required to cleave the peroxide (reaction (3)).[5] Furthermore, the cleavage of the

(1) Kharasch and Brown, THIS JOURNAL, **61**, 2142, 3432 (1939); **62**, 925 (1940); Brown, Kharasch and Chao, *ibid.*, **62**, 3435 (1940).

(2) As expected, the molar yield of hexachloroethane was half of that of 1-chloroapocamphane.

(3) Bartlett and Knox, THIS JOURNAL, **61**, 3184 (1939).

(4) Another possible method of forming the ester RCOOR is by unimolecular decomposition of the peroxide into one molecule of carbon dioxide and one molecule of ester.

(5) Due allowance must of course be made for the fact that the solvent is at a higher concentration than the peroxide. The cleavage of the peroxide by the free 1-apocamphyl radical probably requires less activation energy than is required for the removal of a chlorine atom from a molecule of carbon tetrachloride.

peroxide by the free 1-apocamphyl radical to yield the dimer (bi-1-apocamphyl) (reaction (4)) requires a still higher energy of activation. The stability of the peroxide, its concentration, and the nature of the solvent thus determine the nature and the respective quantities of the reaction products. There is little doubt, however, that the free 1-apocamphyl radical is formed in solution and that this free radical is more reactive than the free trichloromethyl radical, since no products of the cleavage of the peroxide by this latter free radical have been noted.

By a study of the reactions of Grignard reagents with 1-chloroapocamphane in the presence of cobaltous chloride, it is hoped to ascertain whether the free 1-apocamphyl radical is formed in these reactions and, if so, whether it tends to dimerize (reaction (5)), or whether it possesses sufficient energy to remove a hydrogen atom from the ether molecule.

Experimental

Preparation of the Peroxide of Apocamphane-1-carboxylic Acid.—The peroxide of apocamphane-1-carboxylic acid was prepared by stirring a mixture of the acid chloride (3 g.), ether containing 5 drops of water (15 cc.), and sodium peroxide (0.9 g.) for sixteen hours at temperatures between −5 and 10°. The peroxide was taken up in ether, and the solution dried over anhydrous calcium chloride; the ether was then removed in a stream of dry air. The highly stable peroxide was crystallized from methyl alcohol. A sample of it was titrated[6] immediately before use; it proved to be 91 to 96% pure.

Decomposition of the Peroxide of Apocamphane-1-carboxylic Acid in Carbon Tetrachloride.—The peroxide was dissolved in carbon tetrachloride (1:20) and the mixture refluxed for twenty hours. The reaction flask was connected through two traps (the first kept at 0°, the second at −80°) to a train consisting of two soda lime tubes, an ascarite tube, a calcium chloride tube. This train led to a gas collector. No gas passed through the train into the gas collector during the reaction. After the reaction (when a test sample of the solution no longer oxidized potassium iodide), dry nitrogen was swept through the reaction flask and train for one hour. The increase in weight of the soda lime and ascarite tubes was taken as the amount of carbon dioxide produced by the decomposition of the peroxide. This increase averaged 60% of the amount calculated for complete decomposition of the peroxide into carbon dioxide and organic radicals.

About three-fourths of the carbon tetrachloride was removed from the reaction product by fractional distillation through a 12-plate concentric tube column. The last of the carbon tetrachloride was removed from the volatile reaction products by fractional condensation on the vacuum line as follows. A small flask containing the concentrated mixture was connected to a fractionating system consisting of three U-tubes. The one nearest the flask was kept at 0° by ice; the second, at −27° by carbon tetrachloride mush; and the third, at −80° by dry-ice. When the system was highly evacuated, the remaining carbon tetrachloride and some of the more volatile reaction product were distilled into the three U-tubes. Most of the distillate was fractionally condensed in the 0 and −27° tubes. This portion of the material was then distilled back into the flask by surrounding the flask with a −80° bath and heating the two U-tubes with steam. To remove the last traces of reaction product from the carbon tetrachloride solution trapped in the −80° U-tube, this portion of the material was distilled back and forth several times between the first and third U-tubes through the second tube held at −27°.

After all the carbon tetrachloride had been removed, the more volatile fraction of the residual reaction product was sublimed *in vacuo*. To remove the last traces of volatile material, the flask was heated on a steam-bath, until the loss in weight per hour reached a small constant value. The weight of the residue was corrected for this small loss per hour due to sublimation of the less volatile products.

The volatile fraction proved to be composed wholly of hexachloroethane and 1-chloroapocamphane. The analysis of this mixture was simplified by the fact that the chlorine in 1-chloro apocamphane is not removed by the usual polar analytical reagents.[7] Accordingly, the hexachloroethane content of the mixture was determined by treating a sample with sodamide in liquid ammonia. The mixture was stirred overnight, and the residue was titrated for halogen by the Volhard method. Total halogen was determined in a Parr bomb. Using 0.1 *N* silver nitrate solution, a titre of 10.85 cc. for the halogen in the hexachloroethane and a titre of 14.44 cc. for the total halogen was calculated for 0.1 g. of the expected mixture of one mole of 1-chloroapocamphane with one-half mole of hexachloroethane. The values found were 10.68 and 13.63 cc., respectively.

1-Chloroapocamphane was isolated from the mixture by decomposing the hexachloroethane with potassium hydroxide dissolved in diethylene glycol. The 1-chloroapocamphane was then removed by distillation. It was crystallized from dilute methyl alcohol and finally sublimed in high vacuum. It melted sharply at 170 to 171°. The melting point previously reported is 154–156°. However, the material here described was more carefully purified than the material obtained by Bartlett and Knox.

Anal. Calcd. for $C_9H_{15}Cl$: Cl, 22.6. Found: Cl, 22.1.

The non-volatile residue left after the steam distillation contained a small amount of material which was removed by hot 5% sodium hydroxide solution. This material proved to be apocamphane-1-carboxylic acid; it was probably present as an impurity in the peroxide. The oil left after removal of the acid, was dissolved in ligroin and extracted four times with concentrated sulfuric acid. The ligroin solution was then washed with water, dried over anhydrous calcium chloride, and evaporated. The residue was the dimer, bi-1-apocamphyl (m. p. 216–217° (uncor.)).

Anal. Calcd. for $C_{18}H_{30}$: C, 87.80; H, 12.20; mol. wt., 246.4. Found: C, 88.13; H, 12.10; mol. wt., 231.

The sulfuric acid extract was diluted with water. The organic material which separated was taken up in ligroin, and the ligroin evaporated. The residue was saponified with potassium hydroxide in diethylene glycol. This procedure yielded an acid and an alcohol. The acid was identified as apocamphane-1-carboxylic acid by its melting point (211°), its neutralization equivalent (167.2) and the fact that it did not lower the melting point of a known sample of apocamphane-carboxylic acid. The alcohol was identified as 1-apocamphanol by its melting point 160–161° (uncor.). The ester extracted by the sulfuric acid was, therefore, 1-apocamphyl apocamphane-1-carboxylate.

Summary

1. The preparation of the peroxide of apocamphane-1-carboxylic acid is described.

2. The peroxide when heated in carbon tetrachloride solution gave the following reaction products: 1-chloroapocamphane, bi-1-apocamphyl, hexachloroethane, and 1-apocamphanyl apocamphane-1-carboxylate.

3. The mechanism of the decomposition is discussed.

CHICAGO, ILLINOIS RECEIVED SEPTEMBER 17, 1943

(6) Kokatnur and Jelling, THIS JOURNAL, 63, 1432 (1941).

(7) Bartlett and Knox, *ibid.*, 61, 3184 (1939).