of the hydrogenated product was practically quantitative. After crystallization from methanol, 0.45 g. of material was obtained, m. p. 142°.

Demethylation of Compound (I): Preparation of Diethylstilbestrol.—Two grams of compound (I), 5 g. of potassium hydroxide, and 30 cc. of ethylene glycol were sealed in a heavy Pyrex bomb tube at 10^{-5} mm. pressure, and heated at 224° for eighteen hours. After cooling and opening the bomb tube, the reaction mixture was diluted with water, filtered to remove silica, acidified with dilute hydrochloric acid, digested for a short time on the steam-bath, and finally cooled to 0°. The solid which separated was collected on a filter. This crude product was crystallized several times from benzene. By these operations it was separated into a solid and an oil. The solid melted at 165–166°. Its identity with diethylstilbestrol was established by the following criteria: (1) the preparation of the diacetate; (2) the preparation of the dibenzoate; (3) the fact that no depression in melting point was observed when the solid was added to an authentic sample of diethylstilbestrol. The diacetate of this material (crystallized from high-boiling ligroin) melted at 120°. The dibenzoate (crystallized from a mixture of high-boiling ligroin and benzene) melted at 209–211°.

When the residual oil (from the bomb tube reaction) was treated in a sealed tube at 224° with 1.5 g. of potassium hydroxide in 8 cc. of ethylene glycol (as in the first operation), it gave an additional amount of diethylstilbestrol. The total yield of the latter was 1.1 g., or 55.5% of the amount calculated from the weight of compound (I) used.

Preparation of 1-Amino-1-(*p*-methoxyphenyl)-propane.—Anethole hydrobromide (prepared from 20 g. of redistilled anethole according to the directions already described) was poured into liquid ammonia contained in an unsilvered Dewar flask; 2.7 g. of sodamide was then added. After stirring for two hours, a slight excess of sodium was added in small portions. When the excess sodium had reacted with the liquid ammonia (as evidenced by the disappearance of the characteristic blue color), the ammonia was removed by evaporation. The reaction mixture was taken up in water; the solution was made acid and extracted with toluene. Only a minute amount of brown oil was obtained by evaporation of the toluene; this was discarded. The acid aqueous solution was made alkaline with sodium hydroxide and extracted several times with toluene. The combined toluene extracts were dried with a small amount of "Drierite." After the drying agent had been removed by filtration, dry hydrogen chloride was passed into the filtrate. The solid which separated was collected on a filter and purified by solution in absolute alcohol, addition of absolute ether to the solution, and cooling. A snow-white, crystalline material melting at 215° (with decomposition) was thus obtained. The benzoyl derivative of this substance was prepared by the Schotten–Baumann method. When crystallized from aqueous alcohol, it melted at 120°. The total yield of amine hydrochloride was 21 g., or 80% of the amount calculated.

Summary

1. The reactions of α-chloroethylbenzene and α-chloropropylbenzene with sodamide in liquid ammonia have been studied.

2. The preparation of a compound (I) believed to be either 3,4-di-(*p*-methoxyphenyl)-hexene-1 or 1-methyl-2,3-di-(*p*-methoxyphenyl)-3-ethylcyclopropane in 40% yield is described.

3. The preparation of diethyl stilbestrol from (I) has been accomplished.

4. The preparation of 1-amino-1-(*p*-methoxyphenyl)-propane is given.

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

Reactions of Atoms and Free Radicals in Solution. IV. Decomposition of Acetyl Peroxide in Aliphatic Acids—A New Synthesis of Succinic Acid and its Substitution Derivatives

BY M. S. KHARASCH AND MATTHEW T. GLADSTONE

Continuation of previously reported work on the relative reactivities of organic free radicals in solution[1] has led to investigation of the reactions which free radicals formed by decomposition of acetyl peroxide undergo with a number of organic solvents.[2] This paper describes the results obtained when acetyl peroxide is decomposed in liquid aliphatic acids.

When acetyl peroxide, dissolved in glacial acetic acid, is dropped slowly into glacial acetic acid maintained at 95–100°, a rapid evolution of gas indicates that decomposition has set in. This gas was identified as a mixture of methane and carbon dioxide. No hydrogen or unsaturated gases were found. From the reaction mixture, after removal of the acetic acid, there was obtained a residue which, after crystallization from water, was identified as succinic acid by analysis,

[1] Kharasch, Kane and Brown, THIS JOURNAL, **64**, 1621 (1942).

[2] The decomposition of acetyl peroxide in the following solvents has been investigated: (a) diethyl and diisopropyl ethers by Kharasch, Fineman and Brown (unpublished work); (b) carbon tetrachloride and ether chlorinated hydrocarbons by Kharasch, Kane and Brown, THIS JOURNAL, **63**, 526 (1941); (c) acid chlorides by Kharasch and Jensen (unpublished work). The decomposition of other peroxides in the solvents mentioned and in ethers was also investigated.

melting point and neutralization equivalent, as well as by the fact that it did not depress the melting point of an authentic sample of succinic acid.

Acetyl peroxide when decomposed in isobutyric or chloroacetic acid gave tetramethylsuccinic acid and *meso*-dichlorosuccinic acid, respectively. The yield of the dicarboxylic acids was about 42–50%, based upon the acetyl peroxide used (*vide infra*). In addition to the dicarboxylic acids, small quantities (about 5%) of methyl acetate were isolated when acetic and isobutyric acids were used as solvents; chloroacetic acid gave like amounts of methyl chloroacetate. Acetyl peroxide decomposed in acetic anhydride to give a substance which, after treatment with alkali, isolation of the acidic material, and subsequent crystallization from water, was identified as succinic acid.

The experience gained in this Laboratory by decomposing acetyl peroxide in many different solvents justifies the assumption that the peroxide when heated, decomposes as follows

$$(CH_3CO—)_2O_2 \longrightarrow CH_3\cdot + CH_3COO\cdot + CO_2 \quad (I)$$

If the molecules of the solvent are readily attacked by the acetoxy free radicals, then only one mole of carbon dioxide per mole of acetyl peroxide is formed. This relationship holds quantitatively for the decomposition of acetyl peroxide in ethers.[2a] Thus, in diisopropyl ether, only one mole of carbon dioxide is formed per mole of acetyl peroxide. The acetoxy radicals react with the ether molecules in two ways. Some remove hydrogen atoms to give acetic acid; others react with ether molecules to give isopropyl acetate and isopropoxy free radicals which disproportionate to isopropyl alcohol and acetone. Since, in this last reaction, equimolar quantities of ester, alcohol and ketone have been isolated, a common origin for these substances is indicated. On the other hand, if the solvent molecules do not react readily with the acetoxy free radicals, these radicals may decompose into methyl free radicals and carbon dioxide. Varying quantities of carbon dioxide may thus be obtained. These considerations account for the 1.2 to 1.5 moles of carbon dioxide obtained when acetyl peroxide is decomposed in liquid organic acids.

The formation of the dicarboxylic acids from the monocarboxylic acid might be explained in a number of ways. Since the various mechanisms are not equally probable, it is scarcely worth while to enumerate them all. The following scheme appears to account most satisfactorily for the formation of the dicarboxylic acids.

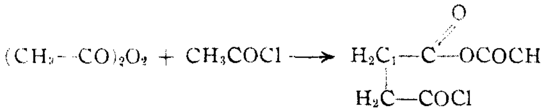
$$(I) \quad (CH_3CO)_2O_2 \longrightarrow CH_3\cdot + CH_3COO\cdot + CO_2$$

$$(II) \quad CH_3COOH + CH_3\cdot \longrightarrow \text{complex} \longrightarrow CH_4 + \cdot CH_2COOH$$

$$(III) \quad \cdot CH_2COOH \xrightarrow{\text{dimerizes}} (—CH_2COOH)_2$$

In this scheme, it is assumed that only the methyl free radicals have sufficient energy to remove hydrogen atoms from the alpha-carbon atoms of the acid. The dimerization of the free radical ($\cdot CH_2$-COOH) might be expected since this radical would probably be stabilized by resonance, and would require a high energy of activation to react with the solvent. These properties in a free radical usually favor dimerization. If the yield of the succinic acids is calculated on the basis of the scheme outlined in equations (I), (II) and (III), it is practically quantitative.

The methyl acetate (5%) found when acetyl peroxide is decomposed in acetic or isobutyric acid, is probably formed from the acetoxy free radicals by disproportionation of acetoxy free radicals into ester and carbon dioxide, and/or by the interaction of the acetoxy free radicals with acetyl peroxide. The latter reaction would probably result in the formation of methyl acetate, carbon dioxide and an acetoxy free radical. To account quantitatively for all the acetoxy free radicals formed in equation (I) is not yet possible.[3] In this connection, the formation of compound (IV)



$$(CH_3—CO)_2O_2 + CH_3COCl \longrightarrow \begin{array}{l} H_2C_1—\overset{O}{\overset{\|}{C}}—OCOCH_3 \\ \;\;\;\;\;| \\ H_2C—COCl \end{array}$$

(IV)

by decomposition of acetyl peroxide in acetyl chloride[2c] is most instructive. We hope to elucidate the reaction further in a future publication.

Experimental

Materials.—Acetyl peroxide was prepared from reagent grade acetic anhydride and sodium peroxide by the method of Gamborjan,[4] as modified by Kharasch, Fineman and Brown.[2a] The solid peroxide was quickly dried *in vacuo*, then dissolved in the appropriate acid and kept, until needed, in the cold. The peroxide content was determined by the method of Kokatnur and Jelling.[5] The glacial acetic acid was purified as described by Kharasch and Hobbs.[6] The acetic anhydride and isobutyric acid were reagent grade chemicals. They were first fractionated

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[3] The present study was interrupted by the call of Lt. Gladstone into Army service.

[4] Gamborjan, *Ber.*, **42**, 4010 (1909).

[5] Kokatnur and Jelling, This Journal, **63**, 1432 (1941).

[6] Kharasch and Hobbs, *J. Org. Chem.*, **6**, 706 (1941).

through an efficient column packed with glass helices and finally distilled *in vacuo*. The chloroacetic acid was distilled *in vacuo* prior to use.

Decomposition of Acetyl Peroxide in Solution.—The procedure used was much the same with all of the solvents. The acid solution of the peroxide was kept in a flask maintained at a low temperature. Thence it was siphoned in small quantities into a dropping funnel. From the funnel, it was introduced below the surface of an additional amount of acid kept in a flask fitted with a reflux condenser. The acid in the flask was maintained at 85–95° by external heating on a steam-bath. After all the acetyl peroxide had been added, heating of the mixture at 85–95° was continued until no more peroxide could be demonstrated in the solution. The gas formed was passed through the condenser to a trap cooled to −80° which usually condensed the methyl acetate formed in the reaction, then through a trap kept at room temperature, and finally through three weighed U-tubes containing soda lime. The residual gas was collected over water. The first two liters of this gas were never used for analyses.

The carbon dioxide formed in the reaction was determined by the increase in weight of the soda lime tubes. The residual gas was shown to be almost pure (97–98%) methane, by vapor pressure measurements at the temperature of liquid nitrogen, and by molecular weight determinations. No hydrogen or unsaturated gases were found, although a careful search for these substances was made.

The reaction mixture remaining in the flask was usually subjected to distillation through a good column. Where chloroacetic acid was used as a solvent, the volatile component of the reaction mixture was removed *in vacuo*. In these experiments, a small amount of methyl chloroacetate distilled first; where acetic or isobutyric acids were used, the methyl acetate was found in the cold trap. The residues remaining in the flask after removal of the solvent were either treated with alkali and the acid recovered by acidification, or else they were crystallized at once from water or some other appropriate solvent.

Decomposition of Acetyl Peroxide in Acetic Acid.—Acetyl peroxide (0.144 mole) in 5 moles of acetic acid decomposed to form 0.22 mole of carbon dioxide, 0.212 mole of methane, 0.0072 mole of methyl acetate, and 0.072 mole of succinic acid. The melting point of the succinic acid thus obtained was 181–182°. The substance did not depress the melting point of an authentic sample of succinic acid. The melting points of various derivatives prepared from the succinic acid isolated in this experiment agreed with those recorded in the literature.

Decomposition of Acetyl Peroxide in Isobutyric Acid.—Acetyl peroxide (0.066 mole) in 2.5 moles of isobutyric acid decomposed to form 0.080 mole of methane, 0.088 mole of carbon dioxide, 0.0072 mole of methyl acetate and 7.7 g. of a residue. From the residue 5.2 g. (0.028 mole) of tetramethylsuccinic acid was isolated. The acid thus obtained melted at 191–192° (recorded m. p. 188°, 190°, 200°). Its neutralization equivalent was 86.5 (calculated neut. equiv. 87). The phenyl imide of acid prepared from this material melted at 85°; the reported melting point of the phenyl imide of tetramethylsuccinic acid[7] is 88°.

Decomposition of Acetyl Peroxide in Chloroacetic Acid.—The decomposition of acetyl peroxide in chloroacetic acid was carried out in the manner already described. The gases formed were carbon dioxide and methane. No methyl chloride was detected, although a careful search for it was made. Upon distillation of the reaction mixture *in vacuo*, a dark residue was obtained. This residue was dissolved in hot alcohol and treated with norite. From the filtrate, upon evaporation of the alcohol, there was obtained a solid which melted at 209–213° (dec.). The previously reported melting point of *meso*-dichlorosuccinic acid is 215° (dec.). The identity of the two substances was further confirmed by the neutralization equivalent and by the fact that the substance found did not depress the melting point of a *meso*-dichlorosuccinic acid prepared by the addition of chlorine to fumaric acid.

Summary

1. The decomposition of acetyl peroxide in acetic and isobutyric acid gives succinic and tetramethylsuccinic acids, respectively. In addition, carbon dioxide, methane and a small quantity of methyl acetate are formed.

2. The decomposition of acetyl peroxide in chloroacetic acid gives *meso*-dichlorosuccinic acid, carbon dioxide and methane.

3. The mechanism of the formation of the dicarboxylic acids is discussed.

CHICAGO, ILLINOIS RECEIVED OCTOBER 5, 1942

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[7] Powers and Gardner, *Ber.*, **23**, 3624 (1890).