[CONTRIBUTION FROM THE NAVAL STORES RESEARCH DIVISION, BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

Synthesis of the Monoacid Chloride and the Monoalkyl Esters of the Maleic Acid Anhydride Addition Product of *l*-Pimaric Acid

BY MORRIS M. GRAFF[1]

In 1932 Arbuzov[1a] and Ruzicka, *et al.*,[2] demonstrated that abietic acid gives an addition product (m. p. 227–228°, $[\alpha]_D$ −25°) with maleic acid anhydride when heated with benzene above 100° in a sealed tube. Later Ruzicka and Bacon[3] and, independently, Wienhaus and Sandermann[4] made the interesting observation that *l*-pimaric acid adds maleic acid anhydride at room temperature resulting in an addition product identical with that of abietic acid. In the present investigation the maleic acid anhydride adduct of *l*-pimaric acid has been the starting material for the synthesis of the alkyl esters of the carboxyl group at carbon atom-1 (C_1). If the adduct is treated with an excess of phosphorus trichloride a monoacid chloride is formed in almost quantitative yield and this can be converted readily into the alkyl esters.

The monomethyl-, ethyl-, *n*-propyl- and *n*-butyl esters of the maleic acid anhydride adduct of *l*-pimaric acid were synthesized by various methods:

I. Esterification of abietic acid with the alcohol followed by reaction with maleic acid anhydride.

II. Reaction of the maleic acid anhydride adduct of *l*-pimaric acid with the alcohol in the presence of sulfuric acid, either (a) in a bomb tube, or (b) by refluxing for a long time.

III. Reaction of the maleic acid anhydride adduct of *l*-pimaric acid with phosphorus trichloride followed by refluxing with the alcohol.

Methods I and II are cumbersome and the yields of ester are low, whereas method III is more rapid and gives pure products in almost quantitative yields.

The experimental evidence shows that the ethyl ester obtained by method III from the monoacid chloride of the maleic acid anhydride adduct of *l*-pimaric acid is identical with the ethyl ester obtained by esterifying abietic acid followed by reaction with maleic acid anhydride. This establishes the fact that phosphorus trichloride reacts only with the carboxyl group at carbon atom-1 and does not affect the anhydride linkage.

Experimental

The maleic acid anhydride addition products used in the synthesis of the monoacid chloride were prepared from WW gum rosin by fusion with maleic acid anhydride[5] or from crude gum at 25° by adding a concentrated acetone solution of the maleic acid anhydride to an *n*-pentane solution of the gum.[6] Repeated recrystallizations of these preparations yielded a product of m. p. 228–230° (cor.).

Anal. Calcd. for $C_{24}H_{31}O_5$: C, 71.96; H, 8.05. Found: C, 71.83; H, 8.10.

Monoacid Chloride of Maleic Acid Anhydride of *l*-Pimaric Acid.—To 10 g. (0.025 mole) of the maleic acid anhydride adduct of *l*-pimaric acid (m. p. 228–230° cor.) in a 100-ml., round-bottom flask was added 6.82 g. (0.050 mole) of phosphorus trichloride. The flask containing the reaction mixture was stoppered with a loose-fitting cork and allowed to remain in the fume cupboard at room temperature for about twenty hours. As the reaction proceeded the adduct changed to a crusty crystalline mass. Suction was applied to the flask to remove most of the unreacted phosphorus trichloride and volatile products formed in the reaction. The monoacid chloride was triturated in ether, transferred to a fritted glass Büchner funnel, washed repeatedly on the funnel with ether, and dried in a vacuum desiccator over calcium chloride and potassium hydroxide pellets. It melted at 165° with decomposition. With this procedure practically quantitative yields of the monoacid chloride are obtained.

Two otherwise workable methods of preparing the alkyl esters of the maleic acid anhydride addition product of *l*-pimaric acid—namely, by esterifying the acid and then treating the resulting ester with maleic acid anhydride; or preparation of the esters by allowing the adduct to react with the alcohol in the presence of sulfuric acid, either under reflux or bomb-tube reaction—are cumbersome and give poor yields.

Preparation of the esters by a method that gives higher yields and obviates the necessity of using esters of abietic acid, is described below in connection with the preparation of the methyl ester.

Methyl Ester of Maleic Acid Anhydride Adduct of *l*-Pimaric Acid.—Fifteen grams (0.0358 mole) of the adduct monoacid chloride was refluxed with 100 ml. (2.52 mole) of methyl alcohol for two hours. About 75 ml. of the alcohol was distilled off and the residue extracted with ether. The ether extract was washed with distilled water until neutral to litmus and dried over anhydrous sodium sulfate. On evaporation of the ether, 14.7 g. (98.9%) of a colorless, glass-like solid was obtained which became crystalline on moistening with solvent. Two recrystallizations from ethyl alcohol and water gave crystals of m. p. 216–217° (cor.); $[\alpha]_D$ −28.9° (5% in chloroform). A melting point determination on a mixture of this material with a preparation obtained by treating methyl abietate with maleic acid anhydride[7] showed no depression.

TABLE I

ALKYL ESTERS OF MALEIC ACID ANHYDRIDE ADDUCT OF *l*-PIMARIC ACID

Alkyl	M. p.,[a] °C.	$[\alpha]_D$[b]	Percentage composition			
			Carbon		Hydrogen	
			Calcd.	Found	Calcd.	Found
Methyl	216 -7	−28.9	72.43	72.31; 72.35	8.27	8.33; 8.41
Ethyl	154.5–5.5	−31.6	72.89	72.87; 72.89	8.41	8.45; 8.57
n-Propyl	146 -7	−31.9	73.27	73.24; 73.34	8.66	8.69; 8.70
n-Butyl	144.5–5.5	−31.2	73.63	73.85; 73.66	8.83	8.80; 8.98

[a] Corrected. [b] 5% in chloroform.

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[1] This paper is the condensation of a thesis submitted by Morris M. Graff in partial fulfillment of the requirements for the M. S. degee, Tulane University, 1946.

[1a] Arbuzov, *J. Gen. Chem.*, *U. S. S. R.*, **2**, 806 (1932).

[2] Ruzicka, Ankersmit and Frank, *Helv. Chim. Acta*, **15**, 1289 (1932).

[3] Ruzicka and Bacon, *ibid.*, **20**, 1542 (1937).

[4] Wienhaus and Sandermann, *Ber.*, **69**, 2202 (1936).

[5] Hovey and Hodgins, *Ind. Eng. Chem.*, **32**, 272 (1940).

[6] Fleck and Palkin, *Ind. Eng. Chem.*, *Anal. Ed.*, **14**, 146 (1942).

[7] Ruzicka, Ankersmit and Frank, *Helv. Chim. Acta*, **15**, 1289 (1932).

The higher-boiling alcohols, being soluble in ether, are apt to be carried through the ether extraction. The presence of these alcohols in the residue inhibits good crystal formation of the ester. This difficulty may be overcome by mixing and melting equimolar concentrations of the acid chloride with the higher-boiling alcohols.

Table I is a composite of analytical data with the procedure just described for the preparation of the esters of the maleic acid anhydride addition product of *l*-pimaric acid.

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Summary

The preparation of the monoacid chloride of the maleic acid anhydride addition product of *l*-pimaric acid is described. The methyl-, ethyl-, *n*-propyl- and *n*-butyl esters of the maleic acid anhydride addition product of *l*-pimaric acid have been prepared by several methods. The synthesis of these esters by the method involving the preparation of the monoacid chloride of the addition product proved less cumbersome than the other methods; it obviated the necessity of using esters of abietic acid, and the yields were practically quantitative.

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The Synthesis and Thermal Decomposition of Di-triethylmethyl, *t*-Butyl Pentamethylethyl and *t*-Butyl 1-Methylcyclohexyl-1 Peroxides[1]

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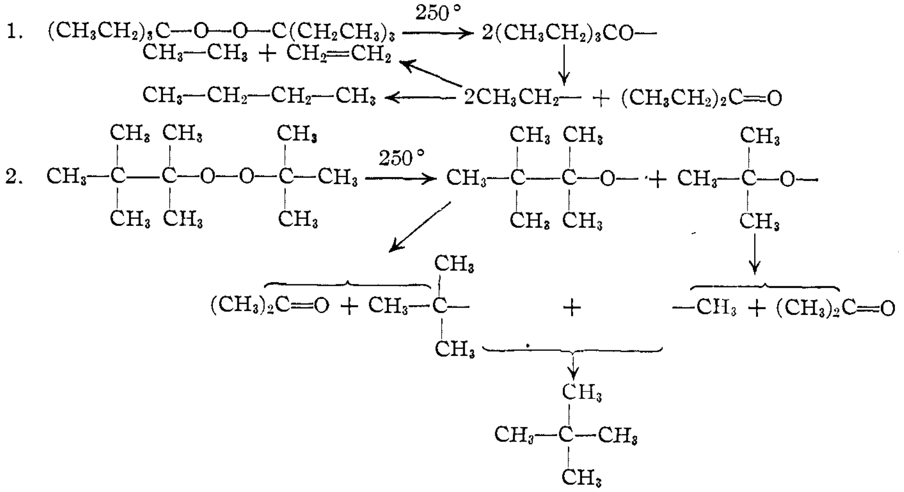
In the previous papers[2] mention was made of the fact that comparatively few tertiary alkyl peroxides and hydroperoxides are known. In order to establish the generality of the original reaction[3] and the mode of the thermal decomposition of di-tertiary alkyl peroxides, a number of higher tertiary alkyl peroxides and hydroperoxides have been synthesized and are herein reported. The ditertiary alkyl peroxides were best prepared from the corresponding tertiary alkyl hydroperoxides and tertiary alkyl hydrogen sulfates. For example, di-triethylmethyl peroxide was prepared from triethylmethyl hydrogen sulfate and triethylmethyl hydroperoxide, *t*-butyl pentamethylethyl peroxide from pentamethylethyl hydrogen sulfate and *t*-butyl hydroperoxide and *t*-butyl 1-methylcyclohexyl-1 peroxide from 1-methylcyclohexyl-1 hydrogen sulfate and *t*-butyl hydroperoxide.

When di-triethylmethyl peroxide was passed through a tube packed with glass wool and maintained at 250°, diethyl ketone and *n*-butane were the main products formed with some ethane and ethylene as by-products. Similarly, *t*-butyl pentamethylethyl peroxide gave, under the same conditions, acetone and neopentane as the chief pyrolysis products. These results may be best interpreted by the following sets of reactions



The pyrolysis of *t*-butyl 1-methylcyclohexyl-1 peroxide (0.134 mole) at 250° yielded acetone (0.117 mole, 87.4%), 3-methylheptanone-2 (0.066 mole, 49.2%), 3,4-di-*n*-butyl hexanedione-2,5 (0.020 mole, 30%) and ethane (0.033 mole, 24.6%) as the only products. These products may be accounted for by assuming a rearrangement of the 1-methylcyclohexyl-1-oxy radical (II) in such a manner that a hydrogen atom migrates from one of the carbon atoms in the cyclohexane ring beta to the oxygen atom simultaneously with the opening of the ring at the other beta carbon atom to form the radical (IV) which may either combine with the methyl radical resulting from the decomposition of the *t*-butoxy radical (III), to form 3-methyl heptanone-2 (V), or dimerize to form 3,4-

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(1) Studies in Organic Peroxides. XI.

(1a) Present address: Union Bay State Chemical Company.

(2) Milas and Surgenor, THIS JOURNAL, **68**, 205, 643 (1946).

(3) Milas, U. S. Patent 2,223,807, Dec. 3, 1940.