The Preparation of *sec*-Alkyl Perchlorates in Strong Acid

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Received August 25, 1970

Covalent esters of perchloric acid have been briefly mentioned in the literature.[1] The lower molecular weight alkyl perchlorates are rather unstable compounds, and preparation of the neat liquids can be quite hazardous.[1] Although some workers have actually distilled them,[1b,2] others have avoided their isolation and used them as formed *in situ.*[3] The most common preparation of alkyl perchlorates is the reaction of an alkyl iodide with silver perchlorate.[1] The

$$RI + AgClO_4 \xrightarrow{\text{solvent}} RClO_4 + AgI$$

reaction of anhydrous perchloric acid with alcohols or olefins is quite hazardous but has been reported,[4,5] and a small amount of perchlorate ester was isolated from the reaction of 9-octadecene or 9-octadecanol with 70% perchloric acid at 100° for 3 hr.[6]

We have developed a new and facile preparation of secondary alkyl perchlorates which does not require use of expensive silver perchlorate or alkyl iodides. The new procedure involves addition of a secondary alcohol or unbranched olefin to a well-stirred emulsion of perchloric acid, sulfuric acid, and an inert hydrocarbon or halocarbon. The acid reagent can be prepared by combining 70% perchloric acid, 96% sulfuric acid, and oleum, or by dissolving lithium perchlorate in 96% sulfuric acid. The formation of isomeric secondary alkyl perchlorates is, in most cases, very rapid and virtually quantitative. The ester products are found in the organic layer, from which they may be isolated (*with caution*) if desired. The composition of the isomeric mixture is dependent on the reaction conditions and can often be made to highly favor one specific isomer.

The key to the synthesis is the use of the nonreactive organic phase in combination with the perchloric acid–sulfuric acid reaction medium. Upon addition to such a system both secondary alcohols and unbranched olefins react rapidly to give either alkyl hydrogen sulfate or alkyl perchlorate. The alkyl perchlorate, being covalent in nature, moves quickly to the organic layer where it is largely protected from further decomposition. The alkyl hydrogen sulfate remains in the acid layer until further reaction produces alkyl perchlorate. However, prolonged maintenance of the emulsion, particularly at room temperature or above, leads to a slow decomposition of the perchlorate, giving products which are typical of those obtained from long exposure of alcohols or olefins to sulfuric acid.[7]

The conditions necessary for the best results are typical of reactions carried out in concentrated sulfuric acid. For maximum yield and minimum isomerization it is advantageous to maintain the reaction temperature just above the freezing point of the emulsion (about 15°). This is particularly true for compounds of composition C_{10} or less (except for isopropyl alcohol, *vide infra*). For optimum yield the acid strength should be kept between 94 and 96 wt % combined acids. With less than 90% acid incomplete reaction occurs and with 100% acid a rather rapid decomposition of perchlorate takes place. An excess of perchloric acid over olefin or alcohol and a large amount of inert organic layer also serve to increase yields. Table I gives typical product yields at two reaction temperatures.

Table I

Yield of Secondary Alkyl Perchlorates

Perchlorate precursor	Alkyl perchlorate yield (%)[a] −10°	25°
Propene	96	*b*
1-Pentene	98	*b*
1-Hexene	99	9
Cyclohexene	89	14
3-Heptene	84	27
1-Decene	100	91
1-Octadecene	100	100
4-Phenyl-1-butene	85	35
5-Methyl-1-hexene	78	*b*
1,7-Octadiene[c]	85	*b*
2-Propanol	6	65
2-Butanol	88	<5
3-Hexanol	98	10
Diisopropyl sulfate[d]	99	*b*

[a] See Experimental Section; the products are often mixtures of *sec*-alkyl perchlorates, the composition of which depends on the conditions of the reaction. [b] Yield not determined. [c] Yield based on both double bonds reacting. [d] Yield based on both isopropyl groups reacting.

Due to the hazardous nature of the perchlorate products, they were not actually isolated and analyzed in pure form, but their presence was established by several observations. First, the hydrocarbon layer of the reaction forms a pyridine–copper nitrate–perchlorate complex in direct proportion to the amount of olefin or alcohol added to the reaction.[8] Careful removal of the solvent from the reaction product of 2-heptene produced an oil which was insoluble in water and heavier than water (the densities are greater than one for perchlorate esters of C_8 or less[2]). When a small portion of the hydrocarbon layer was placed on a preheated hot plate, a small explosion occurred after evaporation of the solvent. Lastly, the nmr spectra in chlorobenzene are completely consistent with those expected for secondary alkyl perchlorates, for example, 2-hexylperchlorate [nmr (PhCl) τ 9.23 (t, 3), 8.78 (d, 3), 8.60 (m, 6), 5.20 (m, 1)] and 2-propyl perchlorate [nmr (PhCl) τ 8.88 (d, 6), 5.05 (m, 1)].

The formation of isomeric mixtures of perchlorates, when permitted by the structure of the reacting molecule, needs some further comment. For this purpose the *sec*-hexyl system serves as an excellent model. Table II contains the isomeric distribution of *sec*-hexyl perchlorates using various hexyl precursors under dif-

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(1) For brief reviews, see (a) H. Burton and P. F. G. Praill, *Analyst (London)*, **80**, 4 (1955); (b) R. D. Stewart, "Perchlorates," J. C. Schumacker, Ed., Reinhold, New York, N. Y., 1960, pp 67, 214.

(2) J. Radell, J. W. Connolly, and A. J. Raymond, *J. Amer. Chem. Soc.*, **83**, 3958 (1961).

(3) H. Buron, D. A. Munday, and P. F. G. Praill, *J. Chem. Soc.*, 3933 (1956).

(4) J. Meyer and W. Spormann, *Z. Anorg. Allg. Chem.*, **228**, 341 (1936).

(5) S. J. Tauber and A. M. Eastham, *J. Amer. Chem. Soc.*, **82**, 4888 (1960).

(6) J. S. Showell and I. S. Shepherd, *J. Org. Chem.*, **34**, 1097 (1969).

(7) N. C. Deno, *Chem. Eng. News*, 88 (Oct 5, 1964).

(8) W. Bodenheimer and H. Weiler, *Bull. Res. Counc. Isr.*, **4**, 316 (1954); *Chem. Abstr.*, **49**, 13022*i* (1955).

Table II

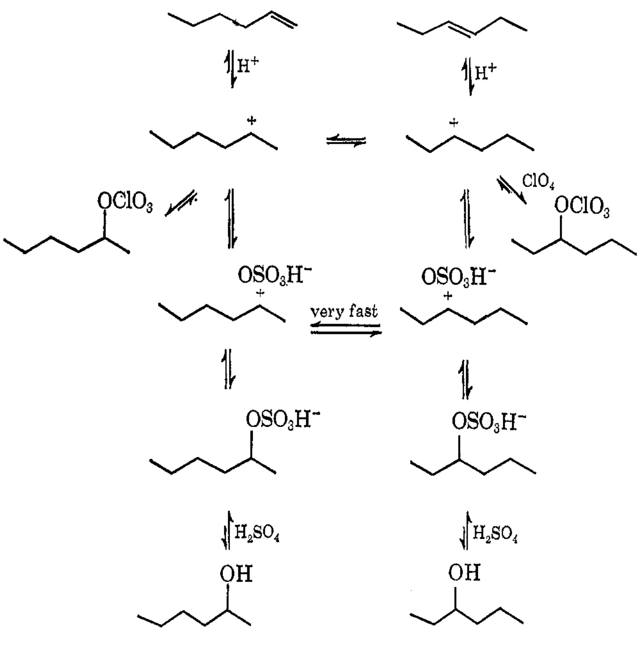
Isomer Distribution of 2- and 3-Hexyl Perchlorates at −15°

Reactant	Isomer distribution (%) 2-isomer	Isomer distribution (%) 3-isomer
1-Hexene	80	20
2-Hexene	45	55
3-Hexene	20	80
2-Hexanol	57	43
3-Hexanol	57	43
1-Hexene[a]	50	50
3-Hexene[a]	50	50

[a] Perchloric acid was added immediately after the olefin was added to a sulfuric acid–chlorobenzene emulsion.

ferent conditions. The reactions were carried out using chlorobenzene as the organic layer, and the isomer distributions were determined by comparing the nmr spectra with spectra of known mixtures of the corresponding hexyl benzoates. Both 2-hexanol and 3-hexanol give the same mixture of hexyl perchlorates regardless of the reaction conditions. In contrast, the hexenes produce isomeric mixtures of perchlorates which are dependent on the olefin used as well as on the reaction conditions. Thus, the addition of olefin to the perchloric acid–sulfuric acid–chlorobenzene emulsion at the lowest temperature possible (−15°) gives mostly the product formed by addition of perchloric acid across the double bond. Higher reaction temperatures or addition of the olefin to a sulfuric acid–chlorobenzene emulsion prior to the addition of perchloric acid produced a mixture of isomers similar to that obtained from the alcohols. Scheme I summarizes the various equilibria which lead to these different product distributions.

Scheme I



There are at least two different pathways leading to perchlorates, one by direct addition across a double bond and the other proceeding through the alkyl hydrogen sulfate. The former route is open only to olefins, whereas both alcohols and olefins (under certain conditions) can react *via* the second pathway. Secondary alcohols react rapidly with 96% sulfuric acid to give the alkyl hydrogen sulfate.[9] The results obtained using 2-propanol (*vide infra*) indicate that the reaction with sulfuric acid occurs in preference to a direct reaction of the alcohol with perchloric acid. The alkyl hydrogen sulfate, once formed, reacts further with perchloric acid to give perchlorate ester at a rather rapid rate. During this sequence of reactions an equilibrium mixture of *sec*-alkyl perchlorates is formed, probably resulting from rapid equilibration through ion pair intermediates. Since the individual perchlorate isomers formed *via* olefins are rather stable toward isomerization in this system, the equilibration must occur prior to the final perchlorate formation. As indicated, olefins can add perchloric acid directly across the double bond without formation of alkyl hydrogen sulfate. Apparently, perchloric acid (or perchlorate ion) can compete very well with sulfuric acid (or bisulfate ion) for the carbonium ion formed on protonation of the olefin. If, however, the olefin is allowed to form the alkyl hydrogen sulfate before the addition of perchloric acid, the resulting product is a mixture of perchlorate isomers, just as from alcohols.

The behavior of 2-propanol requires further comment. It differs from other secondary alcohols in that at low temperature little or no perchlorate ester is formed, whereas at room temperature the yield of perchlorate is considerably greater than it is with the C_4 to C_8 secondary alcohols. The lack of reactivity at low temperatures can be shown to be due to the extremely slow formation of 2-propyl hydrogen sulfate, which can be demonstrated by the nmr spectrum of 2-propanol added to 96% sulfuric acid at −10°. The spectrum contains a methyl doublet due to equilibration between 2-propanol and its conjugate acid. Warming to 0–5° causes a slow change in the spectrum to the methyl doublet of 2-propyl hydrogen sulfate which is located 0.087 ppm upfield of the original doublet. Diisopropyl sulfate reacts rapidly at −10° in the perchloric acid–sulfuric acid system to produce 2-propyl perchlorate quantitatively, demonstrating further that the slow step must be the original esterification of the 2-propanol. The formation of perchlorate ester from 2-propanol at room temperature is due not only to the more rapid rate of formation of 2-propyl hydrogen sulfate but also to the greater stability of the 2-propyl group toward the acid layer, which permits it to survive at this temperature.

The formation of alkyl perchlorates from branched alcohols and olefins has met with only limited success due to the instability of the resulting *tert*-alkyl perchlorate products under the reaction conditions. Primary alcohols react very slowly and apparently give some perchlorate but only after isomerization to secondary structures.

Experimental Section

Preparation of Perchlorate Esters.—Anhydrous lithium perchlorate (3.5 g, 33 mmol) dissolved in 35 ml of 96% H_2SO_4 was added to a 100-ml Morton flask equipped with an overhead stirrer and ice condenser, and cooled in an ice–salt bath. To this was added 15.0 cc of hexane; the contents were emulsified by stirring at 1500 rpm. The reactant olefin or alcohol (1.0 ml, 5–8 mmol) was added by syringe pump over 6 min and the contents of the flask were stirred for an additional 2–10 min. The emulsion was allowed to break and the flask warmed to room tem-

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[9] R. J. Gillespie and J. A. Leisten, *Quart. Rev., Chem. Soc.*, **8**, 40 (1954), and references therein.

perature. Samples of the hydrocarbon layer were then examined for perchlorate content by the colorimetric method described below.

The $LiClO_4$ served only as a source of $HClO_4$ and could be replaced by any inorganic perchlorate which would dissolve sufficiently in H_2SO_4 to liberate the required perchloric acid. Alternatively 70% $HClO_4$ could be added directly to 96% H_2SO_4. If a large amount of perchloric acid was used, it was necessary to add oleum to compensate for the water in the 70% $HClO_4$. The hexane could be replaced with a variety of other substances providing they did not react with H_2SO_4 and the alkyl perchlorate was soluble in them.

Due to the explosive nature of the compounds prepared, the reaction vessel was shielded and isolation of the perchlorate esters was avoided. As long as solvent was present the esters were apparently quite stable. However, if a drop of the hydrocarbon solution was placed on a hot plate, a bright flash was observed after the evaporation of the solvent, illustrating the highly explosive nature of these compounds.

Determination of Perchlorate Esters.—The amount of perchlorate ester present in the hydrocarbon phase of the reaction was estimated by a colorimetric method similar to that described by Bodenheimer and Weiler.[8] A standard solution of the copper nitrate–pyridine complex was prepared by combining 4.8 g of $Cu(NO_3)_2 \cdot 3H_2O$, 50 ml of H_2O, and 11 ml of pyridine and diluting to 1 l. with ethanol. Reference standards were prepared from a titrated solution of 70% $HClO_4$ in EtOH, EtOH, hexane, and the standard solution such that the final solutions contained 5.0 ml of standard, 1.0 ml of EtOH, and 2.0 ml of hexane. The amount of perchlorate formed in a reaction was determined by combining 5.0 ml of standard, 1.0 ml of EtOH, and varying quantities of the hexane layer from the reaction. Additional hexane was added such that the total amount of hexane was 2.0 ml and the tubes were allowed to stand for 1 hr. After centrifuging, the color was compared to the reference tubes. The amount of perchlorate found was then extrapolated to the entire hexane layer. By making 4–6 determinations using different quantities of the hexane layer, an accuracy of $\pm 3\%$ was achieved.

Determination of Nmr Spectra of Alkyl Perchlorates.—The nmr spectra were determined on either a Varian A-60 or T-60 spectrometer. For this purpose the alkyl perchlorates were prepared as described above with the exception that chlorobenzene or hexafluorobenzene was substituted for the hexane layer. The concentration of the perchlorates was 10–20% in the solvent and TMS was used as an internal standard.

On several occasions the nmr was used to estimate the yield of alkyl perchlorate. A weighed portion of toluene was used as the internal standard and combined with a portion of the chlorobenzene layer containing the alkyl perchlorate. The amount of perchlorate was then extrapolated to the entire chlorobenzene layer. This analysis was in very close agreement ($\pm 2\%$) with the one obtained by the colorimetric method.

Registry No.—Perchloric acid, 7601-90-3.

Acknowledgment.—The author wishes to thank Mr. H. Smith Sipple and Mr. Herbert C. Williamson for technical and analytical assistance and Professor Wayland E. Noland for helpful discussions of this work.

Reactions of 2,6-Cycloheptadienone and 2,7-Cyclooctadienone with Primary and Secondary Amines. Synthesis of Tropinones and Pseudopelletierines

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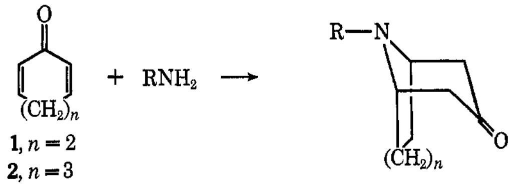
Received November 9, 1970

In his paper describing the synthesis of tropinone (**3a**) by condensation of methylamine with succindialdehyde and acetonedicarboxylic acid, Robinson[1] also noted "that tropinone might result...by the addition of methylamine to a cycloheptadienone...." Nearly 10 years ago, Horák[2] reported the characterization by paper chromatography of tropinone prepared from a large excess of methylamine and 20 mg of a mixture of cycloheptadienones, which had been prepared by treatment of a tropinonium salt with base.[3] In 1965, Garbisch[4] described the preparation of 2,6-cycloheptadienone (**1**), 2,7-cyclooctadienone (**2**), and other cycloalkadienones from their corresponding cycloalkanones. Although four steps are required in Garbisch's synthesis, they are described thoroughly and the overall yields are good. The reasonable accessibility of **1** and **2** made it possible for us to check and extend the alternative synthetic route suggested by Robinson, and we describe here an easily accomplished synthesis of tropinone (**3a**), pseudopelletierine (**4a**), and several of their N-substituted homologs.[5]

Addition of 1 equiv of 2,6-cycloheptadienone[4] (**1**) to a 2 *M* solution of methanolic methylamine at room temperature resulted in a mildly exothermic reaction that could be followed conveniently by examination of the vinyl region in the nmr spectrum. Within 30 min, >95% of the dienone had reacted, and evaporation of the solvent left crude tropinone (**3a**). Use of 2,7-cyclooctadienone[4] (**2**) in place of **1** resulted in a more rapid reaction leading to pseudopelletierine (**4a**).[6] We have also used this method to prepare *N*-benzyl- and *N*-ethylnortropinone (**3b** and **3c**) and *N*-benzylnorpseudopelletierine (**4b**).



1, $n = 2$
2, $n = 3$

3, $n = 2$ **a**, $R = CH_3$
4, $n = 3$ **b**, $R = PhCH_2$
c, $R = C_2H_5$

In addition, we have found that the cycloalkadienones **1** and **2** react rapidly (10 and 1 min, respectively) with equivalent amounts of dimethylamine hydrochloride (2 *M* in methanol) in the presence of dimethylamine (*ca.* 0.1 *M*) to give the methochlorides of **3a** and **4a** (**5** and **6**) directly.[8]

Yields of purified products and their melting or boiling points are summarized in Table I.

Preparation of tropinone, pseudopelletierine, and their N-substituted homologs by condensation of a

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[1] R. Robinson, *J. Chem. Soc.*, **111**, 762 (1917).

[2] V. Horák and P. Zuman, *Tetrahedron Lett.*, 746 (1961); V. Horák, *Collect. Czech. Chem. Commun.*, **28**, 1614 (1963).

[3] J. Meinwald, S. L. Emerman, N. C. Yang, and G. Büchi, *J. Amer. Chem. Soc.*, **77**, 4401 (1965).

[4] E. W. Garbisch, Jr., *J. Org. Chem.*, **30**, 2109 (1965). *Caution!* **1** and **2** are skin irritants.

[5] A related condensation has been described by C. Grundmann and G. Ottman [*Justus Liebigs Ann. Chem.*, **605**, 24 (1957)], who prepared anhydroecgonine by condensing methylamine at 125° with the isomeric cycloheptatrienecarboxylic acids obtained by the Buchner reaction.

[6] The cyclooctadienone obtained by oxidation of 1,5-cyclooctadiene[7] might also be suitable for this and related preparations.

[7] W. J. Farrissey, Jr., U. S. Patent 3,287,427 (Nov 22, 1966); *Chem. Abstr.*, **66**, P115361y (1967).

[8] For other examples of formation of a bicylic system by Michael-type addition of a tertiary amine, see L. A. Paquette and L. D. Wise, *J. Amer. Chem. Soc.*, **87**, 1561 (1965).