yielded, in addition to the expected products **7a** and **11**, large amounts of heptanoic acid, **12** (Equation IV). The formation of **12** could result from cleavage of the C_{11}-C_{12} bond of **10a** or by subsequent oxidation of ketoacid **11** by the perruthenate anion. When RuO_4 was used to oxidize the methyl ester **9b** in organic solvent, a similar product mixture was obtained with the exception that, under these so-called neutral conditions, ~20% of the ketoacid **11** decarboxylated to 2-octanone.

Surprisingly, when ruthenate anion, $RuO_4^{=}$, was allowed to react with acid **9a** at a 1:1 stoichiometry, minor amounts (~25%) of the cleavage acids **11**, **7a** and **12** were also formed in addition to the expected ketoacid **10a**. At higher molar ratios of oxidant to substrate, more of the cleavage products **11** and **7a** predominate (>80% yield). The acids **7a** and **11** seemed to form after the formation of 12-keto-oleic acid **10a**; therefore, the ruthenate anion may attack the enolate anion of acid **10a** with subsequent cleavage of the $C_{11,12}$ and $C_{9,10}$ bonds. This result was unexpected because $RuO_4^{=}$ did not attack isolated double bonds and smoothly converted 12-hydroxystearate to 12-ketostearate.

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New Esterification Method for Resin Acids

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ABSTRACT

The reaction of tetraalkylammonium salts of resin acids using dehydroabietic acid as the model with various alkyl polychlorides was studied as a method for preparing new ester derivatives of rosins. Of the alkyl halides investigated, methylene chloride, 1,1-dichloroethane, 1,2-dichloroethane, trichloroethylene and 1,2,3-trichloropropane reacted with tetrabutylammonium dehydroabietate at moderate temperatures in short reaction times. A number of new esters were identified by NMR, IR and CI-MS. Although many of the primary products were the anticipated monoesters and diesters, some dehydrochlorinated esters were also obtained. The reaction with trichloroethylene resulted in appreciable amounts of dehydroabietic acid anhydride.

INTRODUCTION

Esterification of rosin is difficult because of the hindered tertiary carboxylic acid group of the component diterpene resin acids. Thus, most commercial rosin esters are produced by the reaction of rosin with polyols at high temperature. Such ester formation is energy-intensive and the products are limited to esters of a few available polyols.

The reaction of alkyl monohalides with alkali salts of rosin acids is well known (1,2). However, it is difficult to find a solvent which will dissolve these salts and the alkyl halide without decomposition of reagents and reaction products. Thus, this type of reaction has been of little commercial importance.

Holmberg and Hansen (3) found that the reaction of tetrabutylammonium salts of carboxylic acids with dichloromethane is a convenient method for the preparation of esters of many carboxylic acids. Methylenebisdiesters were obtained in 80% or greater yields by reacting for 4 days in refluxing methylene chloride. These yields were obtained even for such hindered acids as trimethylacetic acid. Application of the tetrabutylammonium salt-alkyl halide procedure to rosins has a potential for energy-conserving preparation of new rosin esters.

EXPERIMENTAL

Reaction

Tetrabutylammonium dehydroabietate (TBA-DeAb) was prepared by mixing 500 mg (1.67 mM) dehydroabietic acid (purity 99+%) dissolved in 10 mL diethyl ether with 2.27 g (1.67 mM) of 19% aq tetrabutylammonium hydroxide. The ether and water were removed with a vacuum evaporator. Other tetralkylamine salts of dehydroabietic acid were prepared in a similar manner.

Reaction of the dehydroabietic acid amine salts with polychloro-compounds was done in reaction vials placed in a constant temperature bath. For example, a 0.6-mL reaction vial containing 20 mg (0.037 mM) of TBA-DeAb and 0.5 mL methylene chloride was placed in the water bath at 40 C for 5 hr. The solution was then transferred to a 10-mL separatory funnel with 5 mL of ether and treated with 2 mL of 5 N H_2SO_4 to quench the reaction. The ether layer was washed with water until neutral, and then dried over $MgSO_4$ After the solvent was removed, the product was analyzed by appropriate methods.

Analysis

Several methods including gas liquid chromatography (GLC), high pressure liquid chromatography (HPLC), infrared (IR) and ultraviolet thin layer chromatography (TLC-UV) were investigated for analyzing the reaction products. The reaction product of TBA-DeAb and methylene chloride was used to evaluate the different methods.

Samples were methylated with ethereal diazomethane and analyzed for methyl dehydroabietate, monochloromethyl dehydroabietate and methylenebisdehydroabietate using the preconditioned gas chromatographic column described by Sinclair et al. (4) for rosin dimers. A 6 ft × 1/8 in. od stainless steel column containing 2% SE-52 on 80/100 Chromosorb W(AW) was programmed from 140 to 310 C at 4 C/min with a postprogram hold of 20 min at 310 C. However, while attempting to obtain response factors, it became evident that the monoester and diester were being decomposed during chromatography. HPLC using a 3.9 mm × 30 cm reversed-phase column (C-18 μ-Bondapak, Waters Associates) gave excellent separation of monoesters from diesters with acetonitrile or methanol as solvent but methyl dehydroabietate and monochloromethyl dehydroabietate were not resolved adequately.

Direct IR analysis of the unquenched reaction solution in the carbonyl region from 1500 to 2000 cm^{-1} provided a quick estimation of reaction products. The carbonyl stretching frequency for TBA-DeAb was observed at about 1565 cm^{-1} and the frequencies of the esters appeared in the region between 1725 and 1750 cm^{-1}.

A TLC-UV method proved to be the most quantitative method among those investigated. The reaction product after quenching was spotted on silica TLC plates and the plates developed with 5% diethyl ether in hexane. The components as detected by UV fluorescence were collected and extracted from the silica with *t*-butyl methyl ether into volumetric flasks. The dehydroabietate aromatic absorption at 276 nm was used to calculate the composition of each component. Approximate kinetic data were obtained by this method. The maximal error was about 15% as estimated from standard mixtures containing pure monochloromethyl dehydroabietate, methyl dehydroabietate and methylenebisdehydroabietate.

Isolation of larger amounts of individual reaction components was accomplished in the same manner.

RESULTS AND DISCUSSION

The comparative reactivity of various amine salts of dehydroabietic acid with methylene chloride was evaluated by the IR method. Triethylammonium-DeAb and tributylammonium-DeAb did not react with methylene chloride at 40 C for 5 hr. However, tetraethylammonium-DeAb and TBA-DeAb reacted well with methylene chloride at the same conditions. Tetramethylammonium-DeAb also reacted but at a slower rate, probably because of partial insolubility of the TMA-DeAb salt.

Comparison of the reaction of TBA-DeAb with methylene chloride, methylene bromide and methylene iodide showed an order of reactivity, I>Br>Cl, analogous to the results of Mills et al. (2).

The reaction of TBA-DeAb with various polychloro compounds was investigated. The physical characteristics of the primary products are summarized in Table I. Of the polychloromethanes, only methylene chloride reacted to a measurable extent; chloroform and carbon tetrachloride did not react at all. The products from methylene chloride were the monochloromethyl dehydroabietate and methylenebisdehydroabietate.

Of the chloroethane derivatives, 1,1-dichloroethane reacted slowly to a give a diester. However, about half of the TBA-DeAb still remained after a 24-hr reaction at 57 C. Reaction of 1,2-dichloroethane and TBA-DeAb at 40 C for 3 hr gave only one compound in quantitative yield corresponding to the monoester, 2-chloroethyl dehydroabietate. Reaction of this monoester for 20 hr with equimolar TBA-DeAb in carbon tetrachloride at 77 C resulted in 60% conversion to the 1,2-ethylenebisdehydroabietate.

When TBA-DeAb was combined with 1,1,2-trichloroethane, the carbonyl absorption of the salt could be seen in the IR spectrum of the solution, but after a 5-hr reaction at 40 C, neither the salt or ester carbonyl absorptions were apparent. Instead, free carboxylic acid was found. A similar result was obtained upon reacting TBA-DeAb with 1,2,3-trichloropropane, but a small yield (ca. 20%) of esters was obtained, one of which was the dehydrochlorinated product, 2-chloro-2-propenyl (i.e., 2-chloroallyl) dehydroabietate. Thus, it would appear that the dehydrochlorination of 1,1,2-trichloroethane is much faster than the esterification reaction but the dehydrochlorination of 1,2,3-trichloropropane is much slower. The chloropropenyl ester probably is formed by either HCl elimination from the dichloropropyl ester or as a concerted reaction with esterification.

Among the chlorinated ethylenes, TBA-DeAb did not react with vinylidene chloride or *trans*-1,2-dichloroethylene at temperatures of 30 and 40 C, respectively. However, the IR spectrum of the reaction solution showed that trichloroethylene reacted extensively with TBA-DeAb. HPLC of the

TABLE I

Primary Ester Products of the Reaction of Tetrabutylammonium Dehydroabietate with Polychloro Compounds

Alkyl halide	Dehydroabietic acid ester products	GC retention (min)	MW[a]	NMR[b] (δ)	IR ($C=O$, cm^{-1})
CH_2Cl_2	Chloromethyl[c]	21.4	349	5.6 (2H,q)	1755
	Methylenebis	53.3	612	5.7 (2H,s)	1755
CH_3CHCl_2	Ethylidenebis	51.6	626	∿6.8 (1H)[d]	1750
CH_2ClCH_2Cl	2-Chloroethyl	23.9	363	3.6 (2H,t) 4.3 (2H,m)	1732
	Ethylenebis	53.0	626	4.3 (4H,s)	1732
$ClHC=CCl_2$	a Dichloroethylene[e]	25.2	395	6.0 (1H,s)	1780 1632 ($C=C$)
$CH_2ClCHC1CH_2Cl$	2-Chloro-2-propenyl	23.9	375	4.7 (2H,s) 5.4 (2H,m)	1736 1640 ($C=C$)

[a] The parent m/e as determined by CI-MS.

[b] Chemical shift position of hydrogens of the O-alkyl group.

[c] In one instance when the solvent was lost during the reaction, dichloromethyl dehydroabietate was found as a minor reaction product: GC 22.4 min; MW 383; NMR 4.1 (1H,s); IR 1730 cm^{-1}.

[d] Hidden among the dehydroabietate aromatic hydrogens; 1.3 (d) for the ethylidene methyl.

[e] Attempts with TBA-acetate and trichloroethylene were unsuccessful to prepare an analogous acetate derivative for comparison with the known 2,2-dichlorovinyl acetate (6) (vinyl H, δ 7.42).

reaction product with the C-18 μ-Bondapak column with acetonitrile as solvent showed 4 major peaks with retention times (1 mL/min flow) of 4.6 (**1**), 6.4 (**2**), 8.2 (**3**), and 9.5 (**4**) min. A few mg of each component were obtained by repetitive chromatography with the analytical column. Both **1** and **3** showed significant hydroxylic absorption in the IR which disappeared upon reaction with bistrimethylsilyl acetamide. The TMS derivative of **3** had a GLC retention of 56 min, whereas a peak could not be seen in the gas chromatogram of TMS-**1**. The purity and quantity of **1** was inadequate for further work at this time. Component **2** was identified as a dichloroethylene ester of dehydroabietic acid by the mass (MS), nuclear magnetic resonance (NMR) and IR spectra. Component **4** was identified as dehydroabietic acid anhydride by IR and NMR comparison with authentic material (dehydroabietic acid anhydride was synthesized by the method described by Selinger and Lapidot [5] for fatty acid anhydrides).

The mechanism of anhydride formation is unclear. The anhydride is not formed by self-condensation of either TBA-DeAb or the monoester in CCl_4, but heating of 5 mg of monoester and 7 mg of TBA-DeAb in 0.5 mL of carbon tetrachloride at 76 C for 15 hr resulted in the conversion of about 20% of the reagents to the anhydride. However, it appears that the major route to anhydride is by reaction of an unstable chloroethylenebisdehydroabietate with TBA-DeAb, because reducing the ratio of trichloroethylene to TBA-DeAb increased the yield of anhydride.

Kinetic Observations

In all of the initial experiments, the alkyl halides were used as solvents and thus were in large (orders of magnitude) excess. Therefore, formation of a monoester for the methylene chloride example (Eq. I) becomes a first-order reaction, and formation of the methylenebis diester (Eq. II) would be a second-order reaction:

$$RCOO^-TBA^+ + CH_2Cl_2 \xrightarrow{k_1} RCOOCH_2Cl \qquad [I]$$

$$RCOO^-TBA^+ + RCOOCH_2Cl \xrightarrow{k_2} (RCOO)_2CH_2 \qquad [II]$$

$$d[A]/dt = -k_1[A] - k_2[A][B] \qquad [III]$$

$$d[B]/dt = k_1[A] - k_2[A][B] \qquad [IV]$$

$$d[C]/dt = k_2[A][B], \qquad [V]$$

where $[A] = [RCOO^-TBA^+]$; $[B] = [RCOOCH_2Cl]$; $[C] = [(RCOO)_2CH_2]$. Then from Equations III, IV and V:

$$2K \ln \frac{K-[B]}{K} = [A] - [A]_0 - [B], \qquad [VI]$$

and

$$K = \frac{k_1}{k_2}.$$

As long as methylene chloride is in large excess, k_1 and the formation of the monoester will be independent of the concentration of TBA-DeAb. The yield of diester can be improved by increasing the value of k_2 (Eq. V) which is accomplished by increasing the concentration of TBA-DeAb, i.e., reducing the solvent (Table II). The plot of the ratio of available chloride vs K was linear as predicted from the above equations.

TABLE II

Composition of the Reaction Product of Methylene Chloride with Varying Concentrations of TBA-DeAb[a]

-Cl/COO-[b]	Monoester (%)	Diester (%)	K
20	0.8	99.2	0.01
100	3.8	96.2	0.04
500	19.8	80.2	0.21
3000	58.9	41.1	1.3

[a] Reaction at 39 C for 5 hr. The TLC-UV method was used to determine the composition. TBA-DeAb was consumed under all conditions.

[b] Ratio of equivalents of total chloride of methylene chloride to equivalents of dehydroabietate carboxyl.

Application of this reaction to rosin and rosin derivatives is the subject of a patent application.

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