Disproportionation of Abietic Acid: I. Iodine Catalyzed Reaction at Low Temperature

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ABSTRACT

Disproportionation of abietic acid in the presence of equimolar iodine was carried out in benzene at 60 C, and the reaction products were continuously determined by gas-liquid chromatography as methyl esters. The major peaks were isolated and characterized by mass, infrared, and nuclear magnetic resonance spectrometry. Four isomers of dihydroabietic acids, dehydroabietic acid, and small amounts of lactones were detected. Electron spin resonance measurement suggested the intermediacy of free radicals.

INTRODUCTION

Disproportionated rosin or tall oil has been investigated by several groups in recent years as an emulsifying agent in the production of styrene-butadiene latexes. In this reaction, palladium (1), sulfur (2), iodine (3-6), or sulfide (7,8) was generally used at an elevated temperature as catalyst. It has also been reported that the disproportionated rosin was composed of dihydro-, dehydro-, tetrahydro-, and secodehydroabietic acids.

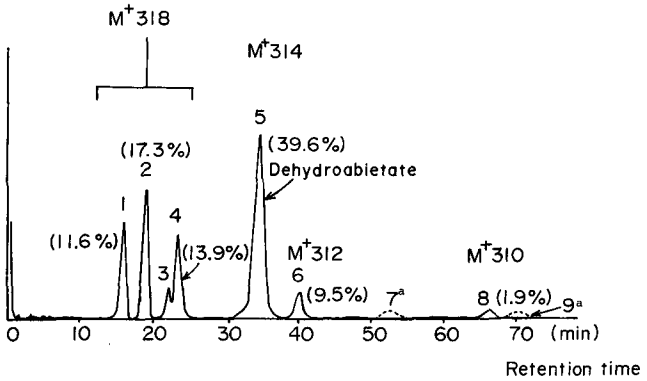

FIG. 1. Gas-liquid chromatographic analysis of disproportionated abietic acid (as methyl esters): column temp 200 C; carrier gas (He) flow rate 20 ml/min. [a]Sensitivity (x 10).

However, we recognized that the disproportionation product of rosin by iodine catalyst at high temperature gave ca. 20 peaks by gas-liquid chromatography (GLC) because of isomerization, cleavage, and decarboxylation. Although it was very difficult to assign structures to all the products and determine reaction mechanisms, it was found that the reaction of abietic acid with a large amount of iodine under mild conditions produced nine major products.

The object of this paper was to investigate the disproportionation of abietic acid with iodine at low temperature.

EXPERIMENTAL PROCEDURES

Materials

Abietic acid was obtained from gum rosin and purified by recrystallization from ethyl alcohol. The purity was 97.2% by GLC; acid number 185.0 (calcd 185.5); mp 160.5-162.0 C. All the chemicals were used without further purification.

Apparatus

GLC was performed with a Yanagimoto G-80 equipped with flame ionization detector and a Yanagimoto GPI-200 electronic digital integrator. Stainless steel column (3m x 3mm diameter) was packed with 20% diethyleneglycol succinate polyester (DESG) on Chromosorb W (60-80 mesh). The composition of the products was determined by normalization of peak areas. Mass spectra were obtained at 70 eV ionization potential with a Hitachi RMU-6E spectrometer. All melting points were determined with a Yanagimoto Micro Melting Apparatus. Infrared (IR) spectra were recorded with a JASCO IR-E spectrometer, and nuclear magnetic resonance (NMR) spectra were obtained with a JEOL LNM-PS-100 spectrometer with tetramethylsilane as an internal standard. Electron spin resonance (ESR) spectra were obtained with a Varian E-LINE EPR Spectrometer System.

Reaction and Analytical Procedures

Disproportionation of abietic acid with iodine was carried out as follows: after addition of 0.42 g (1.65 mmol) of

TABLE I

Relative Retention Times of the Disproportionation Products (as Methyl Esters)

Peak[a] number	Common name	Abbreviation	r_{abiet}
1	Dihydroabietate	DiAb(1)	0.50
2	Dihydroabietate	DiAb(2)	0.58
-	(Palustrate)[b]	Pal	0.64
3	Dihydroabietate	DiAb(3)	0.67
4	Dihydroabietate	DiAb(4)	0.70
-	(Abietate)[b]	Ab	1.00
5	Dehydroabietate	DeAb	1.10
6	Δ^6-Dehydrodehydroabietate	DeDeAb	1.29
7	Dihydroabietic δ-lactone	Lac(δ)	1.68
8	$\Delta^{6,15}$-Dehydrodehydrodehydroabietate	DeDeDeAb	2.21
9	Dihydroabietic γ-lactone	Lac(γ)	2.28

[a]Gas-liquid chromatographic peak number (Fig. 1).
[b]Added as internal standards.

TABLE II

Relative Abundances for Typical Ions in Mass Spectra of Disproportionation Products (as Methyl Esters) (%)

Peak number	Abbreviation	M^+ (m/e)	Base peak (m/e)	M^+	(M^+-15) M^+-CH_3	(M^+-43) $M^+-C(CH_3)2$	(M^+-59) $M^+-COOCH_3$	(M^+-60) $M^+-HCOOCH_3$	(M^+-75) $M^+-CH_3-HCOOCH_3$	(M^+-103) $M^+-C(CH_3)2-HCOOCH_3$	(M^+-117) $M^+-CH_3-C(CH_3)2-COOCH_3$
1	DiAb(1)	318	121	17	3	40	20	6	17	60	8
2	DiAb(2)	318	121	44	12	20	41	14	29	21	11
4	DiAb(4)	318	121	88	13	4	51	24	33	40	0
-	Ab	316	256	92	3	21	26	100	63	50	12
5	DeAb	314	239	12	15	0	3	0	100	5	9
6	DeDeAb	312	237	46	5	0	6	6	100	13	55
8	DeDeDeAb[a]	310	235	55	10	0	23	16	100	0	0

[a]Other characteristic ions, m/e (%): 209(12), 195(44), 141(15).

iodine in benzene into a solution of 0.50 g (1.65 mmol) of abietic acid in 50 ml of benzene, the mixture was maintained at 60 C with stirring under nitrogen atmosphere for 30 min. The reaction mixture was immediately washed twice with 20% solution of sodium thiosulfate in a separatory funnel and dried over anhydrous sodium sulfate. After evaporating the benzene under reduced pressure, the remaining solid was dissolved in ether and methylated with freshly prepared ethereal diazomethane. After removal of the ether and diazomethane, the methylated material was analyzed by GLC at 200 C.

RESULTS AND DISCUSSION

In the study of dehydrogenation of resin acids, we have discovered a number of reduction products of abietic acid. In the presence of an equimolar amount of iodine, abietic acid gave nine abietic acid derivatives on reaction at 60 C for 30 min under nitrogen atmosphere as shown in Figure 1. The relative retention characteristics of the peaks are given in Table I. The structures of the nine derivatives were determined by gas chromatography-mass spectrometry (GC-MS) and NMR spectral analyses. GC-MS analyses were also carried out under the same GLC conditions, and the relative abundances for typical fragment ions were given in Table II. The mass spectra of the four peaks 1-4 showed the same molecular ion at m/e 318, and the characteristic fragment ions at m/e 303 (M^+-CH_3), 275 ($M^+-C[CH_3]_2$), 259 ($M^+-COOCH_3$), and 258 ($M^+-HCOOCH_3$) indicated abietenoate structures.

Retention time data of resin acid methyl esters were compared with the extensive data of Zinkel et al. (9). Methyl dihydroabietates, peaks 1-4 in Figure 1, were preparatively isolated by silver nitrate-silica column (10) and GLC. The NMR spectra of the peaks 1, 2, and 4 are listed in Table III. It has been reported that the mass spectra of the 13α- and 13β-isomers of the 8(14)-abietenoates have a base peak at m/e 275 ($M^+-C[CH_3]_2$) and a stable molecular ion (relative intensity of 60-80%). In contrast, both 13α- and 13β- isomers of 8-abietenoate have a base peak at m/e 243 ($M^+-CH_3-HCOOCH_3$) and a strong peak at m/e 303 (M^+-CH_3) because of the elimination of allylic C-10 methyl (11). Mass spectra data (Table II) suggest that the above compounds are absent.

In consideration of the above data, particularly the signal of C-14 olefinic proton at δ 5.08 (Table III), it was clear that peak 1 was 13-abieten-18-oate (12). In addition to the data in Table II, the mass spectrum of peak 2 exhibited a strong peak at m/e 107 (96%), and the characteristic fragments of m/e 275 and 243 are weak. The NMR signal of olefinic proton at δ 5.32 of peak 2 appeared downfield compared to that of peak 1 (12). From these results, peak 2 was assigned as 13β-abiet-7-en-18-oate.

The NMR spectrum of peak 4 indicated isopropylidene

TABLE III

Proton Chemical-Shifts of Reaction Products
(δ value, 100 MHz, in $CDCl_3$)

Peak number	C-4 methyl	C-10 methyl	Iropropyl methyl(J=5-7Hz)	Olefinic proton	Methyl ester
1	1.17	0.84	0.96	5.08	3.62
2	1.23	0.85	0.91	5.32	3.64
4	1.17	0.85	1.66[a]	---	3.62
5	1.24	1.26	1.18	6.72, 6.85[b] 6.97	3.64
7	1.21	1.08	0.85	---	---
9	1.06	(0.83)[c]	0.88	---	---

[a]Isopropylidene methyls.
[b]Aromatic protons.
[c]C-9 methyl.

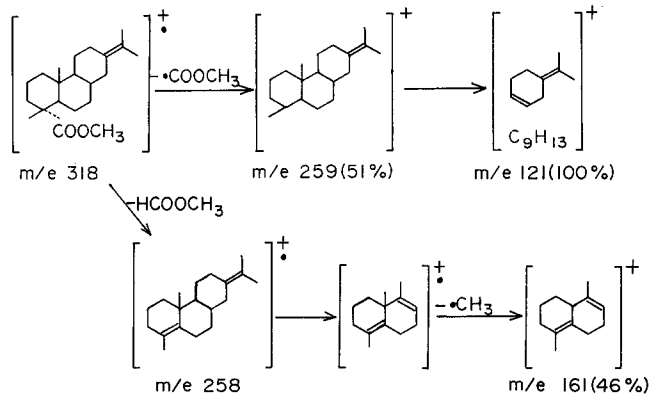

FIG. 2. Mass spectrum of peak 4.

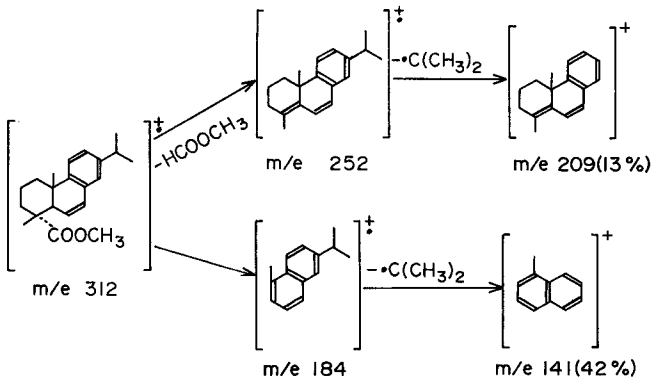

FIG. 3. Mass spectrum of peak 6.

signal at δ 1.66, and olefinic proton was not observed. In addition to NMR, the mass spectrum of peak 4 exhibited a strong M^+ ion at m/e 318 (88%) and the base peak at m/e 121. The low abundance of the peak at m/e 275 (M^+-C[CH_3]$_2$) in the mass spectrum of peak 4 is attributed to the presence of the C13-C15 double bond as shown in Figure 2. These data suggested that peak 4 was 13(15)-abieten-18-oate. GC-MS analysis of peak 3 showed M^+ ion at m/e 318. Though the peak was not well-isolated, it was concluded from its retention time that peak 3 was 7-abieten-18-oate (9).

Peaks 5, 6, and 8 showed base peaks (M^+-CH_3-$HCOOCH_3$) and the characteristic m/e 141 ($C_{11}H_9$) fragment as shown in Figures 3 and 4. Peak 5 was identified as methyl dehydroabietate from GLC, NMR, and GC-MS, which were in good agreement with reported data (9). When the C ring is aromatized, elimination of the C-13 isopropyl group from the molecular ion is not observed (13). In analogy with methyl dehydroabietate, loss of C-13 isopropyl group from any of the molecular ions of peaks 6 (M^+ 312) and 8 (M^+ 310) was not detected (Table II). The fragmentation mechanism to the stable naphthyl ion (m/e 141) was postulated by Chang et al. (11). The mass spectrum (Fig. 3) and the relative retention time of peak 6 agreed closely with 6,8,11,13-abietatetraen-18-oate (9).

In the case of peak 8, the presence of fragment ions of m/e 209 and 195 shows the elimination of isopropenyl group as shown in Figure 4. It may be concluded, then, that the additional double bond is loated at the C15-C16 position.

Reaction product was saponified with KOH solution and extracted with ether. This extract consisted mainly of peaks 7 and 9. These peaks were roughly isolated by column chromatography on alumina. After recrystallizations from ethanol-water, dihydroabietic γ-lactone (peak 9) was isolated (mp 131-132 C, IR 1755 cm^{-1}, mass M^+ 304)

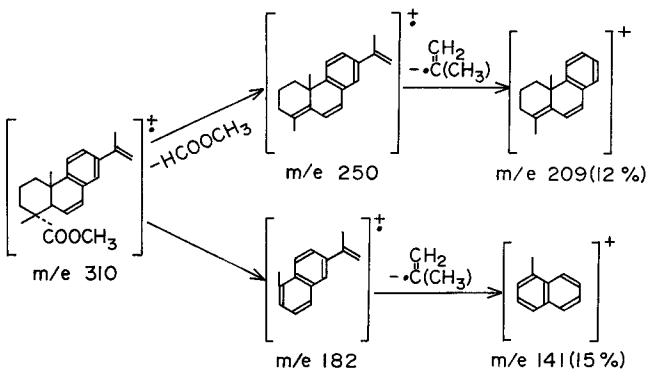

FIG. 4. Mass spectrum of peak 8.

(12,14,15). Column chromatography of the mother liquor on alumina with ether afforded dihydroabietic δ-lactone (peak 7), which was crystallized from methanol (mp 147-148 C, IR 1712 cm^{-1}, mass M^+ 304) (12,14,15).

To clarify the genesis of peaks 6 and 8, dehydroabietic acid was treated with an equimolar amount of iodine under the same reaction conditions as employed with abietic acid. Peaks 6 (7.3%) and 8 (9.2%) were obtained after 60 min. Hydrogenated (via disproportionation) dehydroabietic acid products were not found.

In our study, abietic acid when treated with iodine in the presence of water was readily dehydrogenated to peaks 5 (48.5%), 6 (17.9%), and 8 (10.1%), and hydrogen iodide was observed in the aqueous phase. No dihydroabietic acid derivatives were produced after 30 min. From the facts presented above, dihydroabietic acids were evidently due to the presence of hydrogen iodide which appears to form through dehydrogenation of the conjugated dienoic resin acids.

Although the details of the reaction mechanism of the disproportionation of abietic acid could not be clarified, we assumed the reaction scheme as follows. It is considered that iodine will add to the conjugated double bonds in the first step, and then the elimination of hydrogen iodide produces dehydroabietic acid. On the other hand, addition of hydrogen iodide to abietic acid gives a monoiodo adduct, and dihydroabietic acid, palustric acid, and some dehydroabietic acid may be formed from the monoiodo adduct by intermediacy of free radicals. It is too difficult to clarify the reaction mechanism because of the very complicated reaction mode. However, the existence of many kinds of radical species in this reaction system was observed by measurement of ESR. Further investigation may be necessary to clarify the reaction mechanism.

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