Pyrolyses of Certain Resin Acids at 800°C

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Benzene solutions of levopimaric acid, abietic acid, dehydroabietic acid, and methyl dehydroabietate were pyrolyzed at 800°C on Vycor glass to yield tars containing the following general spectrum of products: toluene, styrene, indene, naphthalene, 2-methylnaphthalene, 2-vinylnaphthalene, acenaphthylene, phenanthrene, fluorene, and 2-phenylnaphthalene. The pyrolysis of methyl dehydroabietate in the absence of benzene indicated that toluene, styrene, indene, fluorene, and 2-phenylnaphthalene were the result of secondary reactions of pyrolysis products with phenyl radicals. Analysis of the products resulting from the pyrolysis of retene, under the same conditions, indicates that the high yield of naphthalene-related products obtained in the resin acid pyrolyzates must arise from A-ring cleavage in the parent molecule before complete aromatization occurs.

The studies of the thermal behavior of resin acids in the past have been largely confined to relatively low temperatures (below 400°C). The work of Arbuzov and Khiamatullins (*1*) along with the observations of other authors (*17*) indicates that the four conjugated dienoic acids—neoabietic, palustric, abietic, and levopimaric—thermally isomerize, and disproportionation occurs in a slow irreversible step to yield dehydroabietic acid. Since low-pressure pot distillation of dehydroabietic acid yielded a pentahydro retene, and heating in the presence of various catalysts converted resin acids to retene and 1-methylphenanthrene (*6*), high-temperature pyrolysis of resin acids would be expected to produce a high yield of phenanthrene-type products.

In the course of our continuing investigation of the effect of heat upon resin acids (*16*, *18*), we have started the first-known study of the reaction of resin acids under high-temperature pyrolytic conditions. In this paper we report that at 800°C on Vycor glass, resin acids fragment to give naphthalene derivatives as major products in contrast to an initially predicted high yield of phenanthrene products.

EXPERIMENTAL

Materials. *Levopimaric Acid.* Levopimaric acid was isolated from pine gum by means of its 2-amino-2-methylpropanol salt (*11*, *15*). The free acid was recrystallized from warm methanol, $[\alpha]^{25}\mathrm{D}$ $-276°$ (C, 2.0 in 95% EtOH) [lit. (*11*) $[\alpha]^{25}\mathrm{D}$ $-276°$].

Abietic Acid. This resin acid was prepared by the mineral acid isomerization of levopimaric acid as described by Schuller et al. (*14*) and recrystallized from methanol; $[\alpha]^{25}\mathrm{D}$ $-102°$ (C, 2.0 in 95% EtOH) [lit. (*14*) $[\alpha]^{25}\mathrm{D}$ $-106°$].

Dehydroabietic Acid. Dehydroabietic acid was isolated from disproportionated rosin by means of its 2-aminoethanol salt according to the method of Halbrook and Lawrence (*5*). The free acid was recrystallized from 95% EtOH; $[\alpha]^{25}\mathrm{D}$ $+60.7°$ (C, 2.0 in 95% EtOH) [lit. (*5*) $[\alpha]^{25}\mathrm{D}$ $+62°$].

Methyl Dehydroabietate. Methyl dehydroabietate was prepared by the reaction of the free acid with diazomethane in diethyl ether. The ester was recrystallized from hot methanol; $[\alpha]^{25}\mathrm{D}$ $+59.8°$ (C, 2.0 in 95% EtOH) [lit. (*8*) $[\alpha]^{26}\mathrm{D}$ $+61°$].

Retene. Crude autooxidized retene was dissolved in a minimum of benzene and passed through a basic alumina column (300 grams; Woelm, W-300, activity grade I). The retene fraction was eluted off with the first 300 ml of benzene to yield 22.4 grams of crude retene (72% by gc analysis). The picrate of the crude product was prepared according to the method of Vogel (*19*) in hot 95% EtOH. The picrate (90% retene) which formed separated upon cooling, was recrystallized from a minimum of hot 95% EtOH to yield 27.9 grams (95% retene by glc) of the picrate; mp 122.5-4°C [lit. (*7*) 123-4°C). The picrate was dissolved in 200 ml of benzene, was passed through 200 grams of basic alumina (Woelm, activity grade I), and was eluted with 100 ml of benzene. The solvent was removed, and the free retene was recrystallized twice from hot 95% EtOH to yield 8.2 grams; mp 98.5-9°C [lit. (*7*) 98-9°C]; uv (95% EtOH) $\lambda_{\max}$ 300.5 (a, 61.5), 288 (a, 45.1), 279.5 (a, 61.5), 258.5 (a, 286), and 251 (a, 238) mμ [lit. (*9*) $\lambda_{\max}$ 300 (a, 60), 287.5 (a, 48), 279 (a, 60), 258.5 (a, 290), and 250 (a, 210) mμ]. (Gc analysis indicated sample to be 97% retene.)

The benzene used as solvent was Baker-analyzed reagent. Toluene, *m*-xylene, cumene, *p*-cymene, and 2-methylnaphthalene were purified by collection from gc; and diphenyl, benzyl, 3,5-dimethylnaphthalene, phenanthrene, 3-methylphenanthrene, and *m*- and *p*-terphenyl were recrystallized from 95% EtOH until gc analysis indicated at least 99% purity.

Apparatus. The pyrolysis apparatus consisted of a vertically mounted Cenco Hevi-Duty Type 70-T electric combustion furnace with a 12-in. heated chamber containing a Vycor glass combustion tube (30 mm o.d. × 32 cm long with a tapered end and a 3- to 4-mm opening) with a 24/40 joint attached to the exit end. The combustion tube was randomly packed with Vycor glass chips with a thermocouple placed in the tube in the center of the heated area. A 24/40 female joint and the thermocouple leads were sealed at the top of the tube with sealing cement coated with liquid silicate. The tube was connected in series to an air condenser, and ice trap, Dry Ice trap, a gas-dispersion trap (containing 15 ml of acetone), and a final Dry Ice trap. (The extensive trapping system was required to trap the aerosol which formed upon cooling of the hot gases.) A Temco portable pyrometer (calibrated by means of a Brown Model 1117 potentiometer) was used to monitor the pyrolysis tube temperature, and a Thermolyn Furnatrol 133 proportional controller maintained the desired temperature. (Selective insulation of the combustion furnace with asbestos paste resulted in about only a 50°C temperature drop at the extreme ends of heated area.)

Typical Pyrolysis Run. A side-arm addition funnel was placed on top of the pyrolysis tube, and nitrogen gas (400 ml/min was forced through the system. When the pyrolysis temperature had stabilized at 800°C, 4 grams of the compound to be pyrolyzed (as a solution of 10 ml of benzene or neat) were placed in the funnel and added dropwise into the pyrolysis tube. When the run was complete, the trapped material was quantitatively removed with benzene, and the samples were

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subjected to gc analysis. In the experiment where methyl dehydroabietate was run neat, it was heated with a heat lamp and added dropwise.

Analysis of Products. Analytical and preparative gc on the resin acid pyrolyzates were carried out on an F&M 500 using a 15-ft × $^1/_4$-in. copper column packed with 5% SE-30 on 60/80 mesh Chromosorb W using a temperature program of 85–275°C at 2.90/min and a He flow rate of 60 ml/min. The products had the following retention times relative to naphthalene: toluene, 0.22; styrene, 0.36; indene, 0.64; naphthalene, 1.00; 2-methylnaphthalene, 1.30; 1-methylnaphthalene, 1.33; 2-vinylnaphthalene, 1.63; acenaphthylene, 1.70; fluorene, 2.08; phenanthrene, 2.50; and 2-phenylnaphthalene, 2.92. The products were trapped off the gc and their uv, ir, and retention time data were identical to authentic samples.

The products in the retene pyrolyzate were analyzed on a 12-ft × $^3/_{16}$-in. copper column packed with 10% OV-17 on 60/80 mesh Gas Chrom Q using a temperature program of 80–280°C at 5°/min and a He flow rate of 100 ml/min. Toluene, styrene, and naphthalene were identified by retention time and uv data. The phenanthrene-related products were collected at 260°C (100 ml/min He) and had the following retention times relative to phenanthrene, 1.00; 2-methylphenanthrene, 1.35; 1-methylphenanthrene, 1.48; 2-vinylphenanthrene, 2.06; retene, 2.86; and 1-methyl-7-vinylphenanthrene, 3.08.

Phenanthrene, 2-methylphenanthrene, and 2-methylphenanthrene yielded ir, uv, and retention time data identical to authentic sample.

2-Vinylphenanthrene. Ir (KBr) ν_{max} 986 (vinyl CH wag), 890, broad (vinyl CH_2 wag and isolated ArH), 810 (2 adj ARH) and 741 (4 adj ArH) cm^{-1}. Uv (95% EtOH) λ_{max} 296.5, 270.5, and 263 mμ, ($CHCl_3$) λ_{max} 303 mμ, 294.5, 290.5 (shoulder), and 270 mμ [lit. (*12*) ($CHCl_3$) λ_{max} 295 and 270 mμ].

1-Methyl-7-vinylphenanthrene. Ir (KBr)ν_{max} 986 (vinyl CH wag), 890, broad (vinyl CH_2 wag and isolated ArH), 810 and 798 (2 adj ArH), and 753 (3 adj ArH). Uv (95% EtOH) λ_{max} 296.5, 270.5, and 263 (shoulder) mμ, ($CHCl_3$)λ_{max} 300, 273, and 265 (shoulder) mμ. The ir and uv data are in accord with the proposed structure. The bathochromic uv shift, when compared with that of 2-vinylphenanthrene, is consistent with increased alkyl substitution at the 1-position of the phenanthrene ring (*2*).

Calculation of % Yields. A benzene solution of weighed amounts of toluene, *m*-xylene, cumene, *p*-cymene, naphthalene, 2-methylnaphthalene, diphenyl, dibenzyl, 3,5-dimethylnaphthalene, phenanthrene, 3-methylphenanthrene, and *m*- and *p*-terphenyl was prepared. The solution was subjected to gc analysis under the same conditions used to analyze the pyrolysis products. A plot of integration area/mg (response/mg) vs. retention time (relative to naphthalene) was prepared and found to be fairly linear with a negative slope. This plot was used to estimate a repsonse factor as a function of retention time for each product appearing on the chromatogram. The measured area of each component was divided by the graphically determined factor before percent by weight yield data was calculated.

RESULTS

The pyrolyses of levopimaric acid, abietic acid, dehydroabietic acid, and methyl dehydroabietate were carried out by passing these compounds in benzene solution, with nitrogen, through a Vycor tube filled with Vycor chips at 800°C and a contact time of 3.9 sec [calculated according to method of Balandin and Tolstopyatova (*3*)]. As expected, considerable carbonaceous and gaseous products (*10*) were produced which were not collected or analyzed. The trapped pyrolyzates yielded about 25% (based on initial weight of material used) of gc analyzable compounds. Comparisons of the yields of the major products identified in this study are given in Table I.

Table I. Major Products from Pyrolyses of Resin Acids at 800°C

	Benzene solution of[a]				
Product	Levopimaric acid	Abietic acid	Dehydroabietic acid	Methyl dehydroabietate	Neat[a] methyl dehydroabietate
	% Yield[b] (Based on Total Weight of Gc Volatile Material Present in Tar)				
Toluene	25	23	16 ± 4.1	13	2.5
Styrene	7	15	17 ± 0.9	16	Trace
Indene	2	5	2 ± 0.4	2	Trace
Naphthalene	34	27	23 ± 2.2	33	20
2-Methylnaphthalene	2	5	4 ± 1.3	3	4
1-Methylnaphthalene	1	3	2 ± 0.8	2	3
2-Vinylnaphthalene	1	2	4 ± 1.1	2	2
Acenaphthylene	5	3	10 ± 2.5	7	15
Fluorene	3	2	3 ± 0.9	2	. . .
Phenanthrene	15	10	8 ± 1.0	11	19
2-Phenylnaphthalene	4	3	7 ± 2.1	5	. . .
	% Yield (Excluding Reaction Products with Solvent)				
Naphthalene	59	54	45	57	40
2-Methylnaphthalene	3	10	8	5	4
1-Methylnaphthalene	2	6	4	3	3
2-Vinylnaphthalene	2	4	8	3	2
Acenaphthylene	9	6	20	12	15
Phenanthrene	26	20	16	19	19

[a] 3.9 Seconds contact time. [b] Products resulting from polymerization of solvent, i.e., biphenyls and terphenyls, are not included in calculating yields.

Even though considerable carbonaceous materials were formed, the standard deviations on the products identified in a number of runs using dehydroabietic acid in benzene show that the system as described does yield reproducible data.

The four compounds studied in benzene solution gave the same general spectrum of products, the major ones being toluene, styrene, indene, naphthalene, 2-vinylnaphthalene, acenaphthylene, phenanthrene, fluorene, and 2-phenylnaphthalene. (Products resulting from the polymerization of solvent—i.e., biphenyl and terphenyls—are not included.)

The analysis of the products from the pyrolysis of methyl dehydroabietate in the absence of benzene showed greatly reduced yield of toluene, styrene, and indene and the absence of fluorene and 2-phenylnaphthalene, implying that these compounds are predominantly produced by the reaction of pyrolysis fragments with phenyl radicals.

Table I shows that naphthalene and its derivatives are the major products in contrast to an initially predicted high yield of phenanthrene-related products. The product composition from the pyrolysis of methyl dehydroabietate in the absence of solvent indicates that the naphthalene derivatives result primarily from the decomposition of the parent resin acid molecule. The decrease in yield of naphthalene in the solvent-free run would imply that approximately 10% of the naphthalene formed in the presence of benzene is due to the reaction of styrene with a C_2 unit, such as a vinyl radical (*4*). Also the presence of benzene as a solvent does not appear to greatly affect any of the primary pyrolytic reaction pathways.

Retene (1-methyl-7-isopropylphenanthrene) was pyrolized under the same conditions as used for the resin acids. The pyrolyzate was analyzed by gc, and the products were identified to be toluene, 5.29% (weight percent of gc volatile portion); styrene, 4.6; phenanthrene, 16.7; 2-methylphenanthrene, 4.8; 1-methylphenanthrene, 20.3; 2-vinylphenanthrene, 16.9; retene, 0.9; and 1-methyl-7-vinylphenanthrene, 19.4.

The retene experiment establishes that the phenanthrene ring system is quite stable under high-temperature pyrolytic conditions and that few naphthalene-related compounds are produced. Therefore, the high yield of naphthalene products during the pyrolysis of the resin acids must arise from cleavage in the A-ring of the parent molecule before complete aromatization occurs. Precedence for rupture of the A-ring is the fact that all compounds studied are converted to dehydroabietic acid under very mild conditions (*17*) and that phenyl nucleus is extremely stable to heat (*4*). Cleavage of the A-ring is most likely facilitated by the ease with which the resin acids undergo decarboxylation [differential thermal analysis and thermogravimetric analysis indicate that resin acids began to readily decarboxylate at 275°C (*13*)].

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LITERATURE CITED

(1) Arbuzov, B. A., Khiamatullins, A. G., *Isvest. Akad. Nauk SSSR, Otdel. Khim Nauk*, 1630 (1961); *CA*, **56**, 13176 (1962).
(2) Askew, F. A., *J. Chem. Soc.*, **1935**, p 509.
(3) Balandin, A. A., Tolstopyatova, A. A., *Gen. Chem.* (*USSR*), **17**, 2182 (1947); *CA*, **42**, 4824i (1948).
(4) Cohen, S., "Progress in Physical Chemistry," Vol. 3, p 1, Interscience, New York, N. Y., 1965.
(5) Halbrook, N. J., Lawrence, R. V., *J. Org. Chem.*, **31**, 4246 (1966).
(6) Hasselstrom, T., *J. Amer. Chem. Soc.*, **63**, 1164 (1941).
(7) Haworth, R. D., Letsky, B. M., Mavin, C. R., *J. Chem. Soc.*, **1932**, p 1784.
(8) Joye, N. M., Jr., Lawrence, R. V., *J. Chem. Eng. Data*, **12**, 279 (1967).
(9) Kanno, H., Schuller, W. H., Lawrence, R. V., *J. Org. Chem.*, **31**, 4138 (1966).
(10) LaLande, W. A., Jr., *Ind. Eng. Chem.*, **26**, 678 (1934).
(11) Lloyd, W. D., Hedrick, G. W., "Organic Synthesis," **45**, 64 (1965).
(12) Price, C. C., Halpern, B. D., *J. Amer. Chem. Soc.*, **73**, 818 (1951).
(13) Schuller, W. H., Conrad, C. M., *J. Chem. Eng. Data*, **11**, 89 (1966).
(14) Schuller, W. H., Takeda, H., Lawrence, R. V., *ibid.*, **12**, 283 (1967).
(15) Summers, H. B., Jr., Lloyd, W. D., Hedrick, G. W., *Ind. Eng. Chem., Prod. Res. Develop.*, **2**, 173 (1963).
(16) Takeda, H., Kanno, H., Schuller, W. H., Lawrence, R. V., *Ind. Eng. Chem.*, **7**, 186 (1968).
(17) Takeda, H., Schuller, W. H., Lawrence, R. V., *J. Chem. Eng. Data*, **13**, 579 (1968).
(18) Takeda, H., Schuller, W. H., Lawrence, R. V , *J. Org. Chem.*, **34**, 1459 (1969).
(19) Vogel, A. I., "Practical Organic Chemistry," 2nd ed., p 500, Longmans, Green, New York, N. Y., 1951.

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Preparation of Dimethyl α,α′-Bis(diethylphosphono)adipate and α,α′-Bis(diethylphosphono)adipamide

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Dimethyl α,α′-bis(diethylphosphono)adipate and α,α′bis(diethylphosphono)adipamide have been prepared by conventional methods. Some nuclear magnetic resonance and infrared data have also been described.

Research is being conducted at the Southern Regional Research Laboratory to prepare new compounds containing phosphorus for use in the development of flame-retardant finishes for cotton products. One class of compounds of interest was dicarboxylic acid derivatives containing a phosphono group attached to the α,α′ carbon atoms.

The only α,α′-bis(diethylphosphono) derivatives of a dicarboxylic acid reported are those for succinic acid, in which case acetylenedicarboxylic acid was used as the starting material (*5, 7*). Because this method is not applicable with dicarboxylic acids containing more than four carbon atoms, the objective of the present investigation was to prepare α,α′-bis(dialkylphosphono)dicarboxylic acid esters and amides by an alternative route.

Esters of α-(diethylphosphono)alkylcarboxylic acids have been prepared by the Arbuzov reaction of triethyl phosphite and the ester of the appropriate C_4–C_{18} straight-chain α-

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