Ortho, meta and para compounds are ordinarily distinguished by utilizing certain longer wave length bands. Thus, it is well known that para compounds nearly always have a strong absorption band at 12–12.5 μ, meta compounds at 12.5–13 μ, and ortho compounds at 13–13.5 μ. (See for example, Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).) This appears to be true also for the compounds discussed here. However, the presence of the trimethylsilyl group introduces a very considerable complication. Other work[12] has established that the trimethylsilyl group usually is characterized by very strong absorption at about 12 μ.

In general, organo-silicon compounds are best studied spectrally with optical paths equivalent to those employed for the spectra of this paper. Ordinarily, however, organic compounds are best studied for structural features at optical paths 5 to 10 times greater than these. Hence, the usual functional bands established for the infrared spectra of many organic compounds appear abnormally weak unless this factor of optical path is kept in mind. It is a nearly general feature of organosilicon compounds that many of the absorption bands in their infrared spectra are 5 to 10 times as intense as those of other organic compounds for equivalent optical paths. With this in mind, it is not too unreasonable to point out that in the ortho, meta and para systems studied here the characteristic longer wave length bands do appear as expected. The tolyl system, for example, has weaker bands at 12.5 μ for the para, 12.86 μ for the meta, and a strong band at 13.3 μ for the ortho. This latter band is probably misleading because the situation is further obscured by the fact that the spectra all show an intense band in the interval 13.3–13.5 μ which we have not attempted to interpret as characteristic of a particular mode of vibration. It may be supposed that the band characteristic of *o*-tolyl is completely merged in a much stronger band characteristic of the unexplained vibration. A similar ordering is readily discernible in the other isomer systems.

Of course, because of the complications introduced by the trimethylsilyl group, the longer wave length bands for ortho, etc., are really explained in a rather *ad hoc* fashion, reducing the usefulness and reliability of such bands for functional determinations.

It is of interest to note that the methyl group is well-marked by an absorption band near 8 μ as noted for other silicon compounds.[13,14] Detailed examination of the individual spectra, and intercomparison, shows that any considerable contamination of one isomer by others can be ruled out by utilizing particular infrared bands in the manner usual for quantitative infrared analysis. The spectra as presented in this paper do not, necessarily represent the optimum conditions for best quantitative analysis since they were chosen to bring out certain features associated with structural problems.

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[12] Wright and Hunter, THIS JOURNAL, **69**, 803 (1947).

[13] Young, Koehler and McKinney, *ibid.*, **69**, 1410 (1947).

[14] Young, Servais, Currie and Hunter, *ibid.*, **70**, 3758 (1948).

MIDLAND, MICH. RECEIVED AUGUST 28, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE HERCULES POWDER COMPANY AND THE UNIVERSITY OF MARYLAND]

Derivatives of Dehydroabietic Acid

BY YOLANDA T. PRATT[1]

Derivatives of dehydroabietic acid (I) with α-hydroxyethyl, vinyl, succinoyl, chloromethyl, methylol and aminomethyl groups at the 6-position have been synthesized. An oxidation product of dehydroabietic acid has been identified as the 9-keto derivative (XIII) and 6-carboxydehydroabietic acid (III) and 6-chloromethyldehydroabietic acid (VIII) have been oxidized to 9-keto-6-carboxydehydroabietic acid (XIV).

Dehydroabietic acid (I), obtained by the dehydrogenation of resin acids[2,3] or dehydrogenation and hydrolysis of resin acid esters,[4] is a readily available acid containing a partially saturated phenanthrene nucleus. The aromatic ring serves as a reactive center for the introduction of functional groups leading to a wide variety of potentially useful products. Previous work in this field[3] has shown that the aromatic ring may be satisfactorily sulfonated, nitrated or acetylated at the 6-position. In the present study a number of derivatives have been obtained by way of the Friedel–Crafts and Blanc chloromethylation reactions. An oxidation product of dehydroabietic acid (I) has been identified as the 9-keto derivative (XIII) and both 6-carboxydehydroabietic acid (III) and 6-chloromethyldehydroabietic acid (VIII) have been oxidized to 9-keto-6-carboxydehydroabietic acid (XIV).

Methyl 6-carboxydehydroabietate had previously been obtained in low yield from methyl 6-acetyldehydroabietate (II) by means of the iodoform reaction.[3] The over-all yield for the conversion of II to the dicarboxylic acid (III) has been raised to 80% by application of King's[5] procedure which involves hydrolysis of the β-ketoalkylpyridinium iodide (VI). A good yield of methyl 6-α-hydroxyethyldehydroabietate (IV) was obtained by the catalytic hydrogenation of the acetyl derivative (II). Upon dehydration the hydroxy compound (IV) yielded crude methyl 6-vinyldehydroabietate (V), which readily polymerized to a hard resin.

The keto dicarboxylic acid VII was obtained in about 50% yield when dehydroabietic acid (I) was

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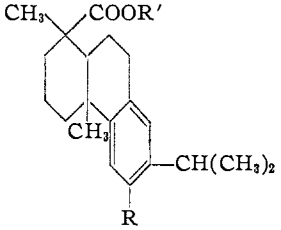
[1] Department of Chemistry, University of Maryland.

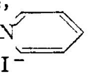
[2] E. E. Fleck and S. Palkin, THIS JOURNAL, **60**, 921 (1938).

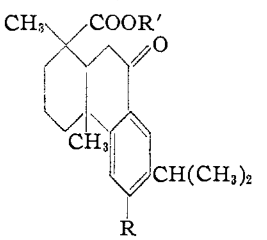
[3] L. F. Fieser and W. P. Campbell, *ibid.*, **60**, 2631 (1938); **61**, 2532 (1939).

[4] Unpublished results, Hercules Experiment Station.

[5] L. C. King, THIS JOURNAL, **66**, 894 (1944).



I, R = H; R′ = H
II, R = $COCH_3$; R′ = CH_3
III, R = COOH; R′ = H
IV, R = $CHOHCH_3$; R′ = CH_3
V, R = $CH{=}CH_2$; R′ = CH_3
VI, R = $COCH_2$—  R′ = CH_3
VII, R = $COCH_2CH_2COOH$; R′ = H
VIII, R = CH_2Cl; R′ = H
IX, R = CH_2OH; R′ = H
X, R = CH_2NH_2; R′ = H
XI, R = CH_2Cl; R′ = CH_3
XII, R = $COOCH_3$; R′ = CH_3



XIII, R = H; R′ = H
XIV, R = COOH; R′ = H
XV, R = $COOCH_3$; R′ = CH_3

treated with succinic anhydride in the presence of aluminum chloride. It is assumed that the succinoyl group, like the acetyl group and the chloromethyl group (see below), enters predominately at the 6-position.

By means of the Blanc reaction dehydroabietic acid (I) was converted in almost quantitative yield to crude 6-chloromethyldehydroabietic acid (VIII)[6] which contained 85% of the theoretical amount of chlorine. This product was not purified but was converted to the crystalline methyl ester (XI). The location of the chloromethyl group was established by means of oxidation experiments described below.

When an attempt was made to hydrolyze the crude product VIII to the 6-methylol compound (IX) aqueous alkali some interaction of the chloromethyl group with the potassium salt of the carboxyl group apparently occurred and the resulting esters were not hydrolyzed under these mild conditions. Upon hydrolysis of the chloromethylation product in a solution of potassium hydroxide in diethylene glycol at the reflux temperature there was obtained a low-melting resin, probably because of the formation of ethers with the solvent. The crystalline hydroxy acid IX was, however, obtained in 61% yield (calculated from dehydroabietic acid) when VIII was first treated with aqueous alkali and the crude mixture thus obtained was heated with potassium hydroxide in diethylene glycol containing a small amount of water.

The hydrochloride of 6-aminomethyldehydroabietic acid (X) was prepared in 48% yield (based on dehydroabietic acid) by treatment of the crude chloromethyl compound (VIII) with hexamethylenetetramine and hydrolysis of the resulting derivative. The hydrochloride was converted to the free base and its acetate.

Previous to the work reported here, Dr. Arthur Drake[7] found that when an aqueous solution of sodium dehydroabietate was treated with oxygen the resulting reaction mixture showed strong absorption in the ultraviolet and the spectrum was very similar to that of methyl 6-acetyldehydroabietate (II, Fig. 1). It appeared, therefore, that the mixture contained a relatively large proportion of a product related to this acetyl derivative.

In the present investigation it was found that a mixture with essentially the same absorption spectrum was obtained when alkaline permanganate rather than oxygen was used as the oxidizing agent. The major product, a carbonyl compound, was isolated by means of Girard Reagent T[8] in 48% crude yield and crystallized in 33% yield (calculated from dehydroabietic acid). The presence of a keto group rather than an aldehyde group was indicated by the fact that the compound did not reduce Tollens reagent. Upon reduction by the Wolff–Kishner method the oxidation product was converted back to dehydroabietic acid (I). The results of the elementary analyses of the oxime and the neutral equivalent and the analytical data for the carbonyl compound indicated that the latter was a keto monocarboxylic acid with the formula $C_{20}H_{26}O_3$.

By analogy with the oxidation of tetralin to tetralone and numerous similar oxidations[9] it would be expected that dehydroabietic acid would oxidize at a carbon atom adjacent to the aromatic ring. The high absorption coefficient of the oxidation product as compared with that of dehydroabietic acid and the marked similarity of the spectrum (Fig. 1) to that of the methyl 6-acetyldehydroabietate (II) indicated that the double bond of this oxidation product was conjugated with the aromatic ring.[10] Since the introduction of a conjugated carbonyl group at any position other than position 9 would require the loss of at least one carbon atom, structure XIII has been assigned to the keto acid.

By means of the above method of oxidation it was established that the chloromethyl group of the product from the Blanc reaction (VIII) is located at the 6-position since both VIII and 6-carboxydehydroabietic acid (III) yielded the same oxidation product (XIV) as shown by mixture melting point determinations on the dimethyl ester (XV). The neutral equivalent and the results of elementary analyses of the oxidation product and two derivatives indicated that it was a keto dicarboxylic acid with the formula $C_{21}H_{26}O_5$.

Evidence for the position of the carbonyl group in this product was obtained by comparing the ul-

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[6] Y. T. Pratt (to Hercules Powder Company), U. S. Patent 2,472,437 [*C. A.*, **43**, 6665 (1949)].

[7] A. E. Drake (to Hercules Powder Company) U. S. Patent 2,434,643 [*C. A.*, **42**, 2786 (1948)].

[8] A. Girard and G. Sandulesco, *Helv. Chim. Acta*, **19**, 1095 (1936).

[9] After this work had been written up for publication a paper appeared by A. Brossi, H. Gutmann and O. Jeger, *Helv. Chim. Acta*, **33**, 1730 (1950), in which the analogous oxidation of the hydrocarbon obtained upon the removal of the carboxyl group of dehydroabietic acid is described. The absorption spectrum of their product strongly resembles that of XIII.

[10] T. W. Campbell, *et al.*, THIS JOURNAL, **69**, 680 (1947).

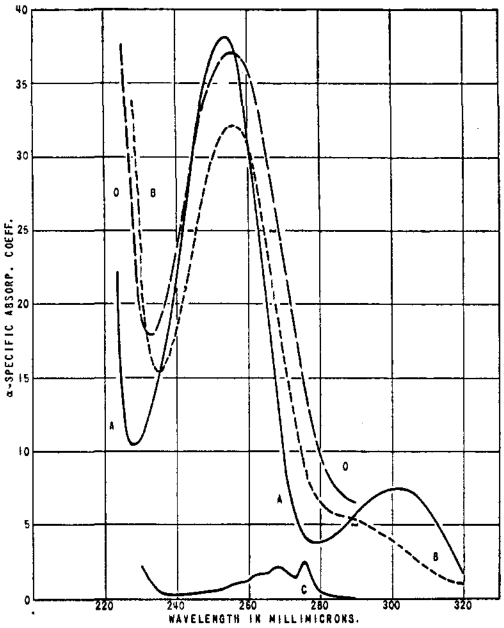

Fig. 1.—Ultraviolet absorption spectra: A, ketodehydroabietic acid (XIII); B, methyl 6-acetyldehydroabietate (II); C, dehydroabietic acid (I); D, oxime of ketodehydroabietic acid (oxime of XIII).

traviolet absorption spectrum of its dimethyl ester (XV) with that of the dimethyl ester of 6-carboxydehydroabietic acid (XII) as shown in Fig. 2. The increase in intensity and the bathochromic shift resulting from the introduction of the carbonyl group indicate that the carbonyl group is conjugated with the aromatic ring[10] and therefore occupies position 9 (XV). Further support for structure XV for the keto dicarboxylic acid ester is seen in the close similarity of the curve to that for 9-ketodehydroabietic acid (XIII, Fig. 1).

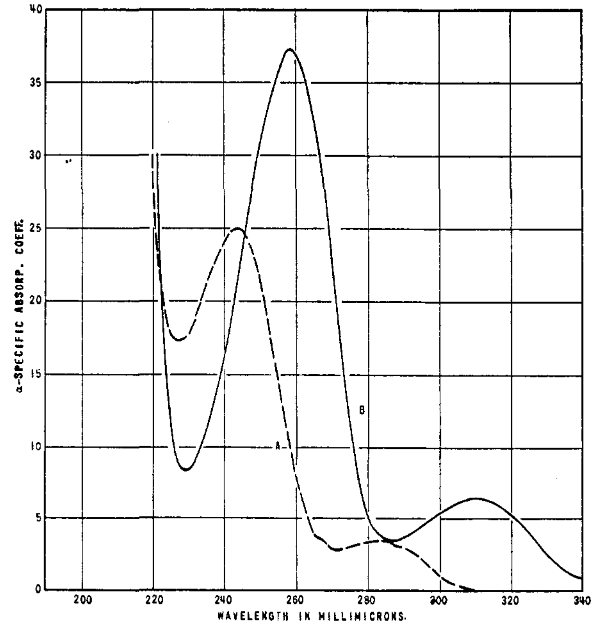

Fig. 2.—Ultraviolet absorption spectra: A, methyl 6-carbomethoxydehydroabietate (XII); B, methyl 9-keto-6-carbomethoxydehydroabietate (XV).

Experimental[11,12]

Methyl 6-Acetyldehydroabietate (II).—This compound was prepared from methyl dehydroabietate by the method of Fieser and Campbell[3] except that tetrachloroethane was used as the solvent and the reaction was allowed to proceed at room temperature for 40 hours after all of the aluminum chloride had been added. Yields of the 6-isomer ranged from 75 to 82%.

6-Carboxydehydroabietic Acid (III).—A solution of 3.56 g. of methyl 6-acetyldehydroabietate (II) in 7 ml. of pyridine was warmed on the steam-bath with 2.54 g. of iodine for 1.5 hours. After the reaction mixture had been allowed to stand overnight, the excess pyridine was removed under reduced pressure and the residue was dried under vacuum at 130°. This crude product (7.50 g.) was heated under reflux for one hour in 100 ml. of a 1 *N* solution of potassium hydroxide in diethylene glycol which contained 1 to 2 ml. of water. The dark solution was diluted with water, acidified with hydrochloric acid and extracted with ether. The product was extracted from the ether with dilute sodium bicarbonate and the resulting aqueous solution was almost completely decolorized by warming with Norite A. It was then acidified to give a colorless crystalline product in yields of 70 to 80%. *Anal.* Calcd. for $C_{21}H_{28}O_4$: neut. equiv., 172. Found: neut. equiv., 173. The product was recrystallized from ethanol and water; the melting point was above 280°.

This compound was converted to the dimethyl ester by treatment with diazomethane. The melting point of this ester and of mixtures with the dimethyl ester prepared from methyl 6-carboxydehydroabietate obtained by the iodoform reaction according to the method of Fieser and Campbell[3] was 112–113°.

Methyl 6-α-Hydroxyethyldehydroabietate (IV).—A solution of 29.8 g. of II in 600 ml. of glacial acetic acid was hydrogenated at 29° and at atmospheric pressure over platinum oxide (1.5 g.) until one mole of hydrogen per mole of ketone had been absorbed (1.75 hours). After filtration the solution was diluted with 1500 ml. of water and the crystalline precipitate was filtered off and dissolved in ether. The ether solution was washed with dilute sodium bicarbonate and water. It was then shaken with anhydrous sodium sulfate and evaporated to dryness. The colorless residue was recrystallized from petroleum ether. The first crop (22.6 g.) melted at 103–105° and the second crop (3.5 g.) at 101–103°; total yield 90%. Upon further recrystallization there was obtained a product which melted at 104–105°. *Anal.* Calcd. for $C_{23}H_{34}O_3$: C, 77.1; H, 9.6. Found: C, 77.1; H, 9.7; $[\alpha]^{25}_{D}$ +70° (1% solution in absolute ethanol).

This alcohol was dehydrated by heating for one-half hour at 145° with $^1/_5$ its weight of fused potassium bisulfate and a trace of hydroquinone while the water vapor was removed under reduced pressure. The product was then dissolved in ether and the ether solution was washed with water and dried. Upon evaporation of the solvent at room temperature a low-melting crude product was obtained. The bromine number was 38 (theory, 47). The ultraviolet absorption spectrum in methanol (specific absorption coefficient λ_{max} 252 mμ, α 31.8) was very similar to that of methyl 6-acetyldehydroabietate (λ_{max} 256 mμ, α 32.0) except for a slight shift toward the shorter wave lengths. The curve for the intermediate α-hydroxyethyl derivative (λ_{max} 268 mμ, α 2.8) resembled that for dehydroabietic acid. A sample of the material prepared in the absence of hydroquinone was polymerized to a hard resin by warming at 70° with a trace of benzoyl peroxide.

6-Succinoyldehydroabietic Acid (VII).—A mixture of 10 g. of dehydroabietic acid, 50 ml. of tetrachloroethane, 3.5 g. of succinic anhydride and 13.3 g. of aluminum chloride was stirred at room temperature for nine days. The dark viscous reaction mixture was treated with hydrochloric acid and ice and the tetrachloroethane was removed by steam distillation. The hot supernatant liquid was separated by decantation to remove dissolved succinic acid and the pale yellow residue was dissolved in ether. The ether solution was washed with water, dried and concentrated to a small volume, whereupon the product crystallized in 49% yield

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(11) All melting points are corrected.

(12) Microanalyses by the Analytical Group of the Hercules Experiment Station and Dr. Eleanor Werble at the University of Maryland. The values given are averages of duplicate determinations.

(6.55 g.). The neutral equivalent of this product was 204. A sample recrystallized from aqueous ethanol for analyses became red at about 200°, melting completely at about 240°. *Anal.* Calcd. for $C_{24}H_{32}O_5$: C, 72.0; H, 8.1; neut. equiv., 200. Found: C, 72.2; H, 8.1; neut. equiv., 202; $[\alpha]^{25}D$ +74° (1% in absolute ethanol).

6-Chloromethyldehydroabietic Acid (VIII).—A solution of 25 g. of dehydroabietic acid, 3.3 g. of paraformaldehyde and 5.2 ml. of 85% phosphoric acid in 50 ml. of glacial acetic acid was heated with vigorous stirring at 105–110° for 11 hours while treated with a stream of gaseous hydrogen chloride. The reaction mixture, which had separated into two layers, was diluted with water and extracted with ether. The ether extract was washed with water and dried over Drierite. Upon evaporation of the solvent there was obtained a resinous, pale yellow residue which was converted under reduced pressure to a froth that could be powdered and dried. The crude material (27.2 g.) did not yield a crystalline product. *Anal.* Calcd. for $C_{21}H_{29}O_2Cl$: Cl, 10.2. Found: Cl, 8.7.

Methyl chloromethyldehydroabietate (XI) was prepared by treatment of the crude product VIII with diazomethane. It crystallized from petroleum ether as large prisms; after several recrystallizations the melting point was 118–120°. *Anal.* Calcd. for $C_{22}H_{31}O_2Cl$: C, 72.8; H, 8.6; Cl, 9.8. Found: C, 72.9; H, 8.7; Cl, 9.8.

6-Methyloldehydroabietic Acid (IX).—Five grams of crude chloromethyldehydroabietic acid (VIII) was heated under reflux for 1.5 hours with 60 ml. of 5% potassium hydroxide. The acidified solution was extracted with ether and the extract was washed with water and saturated sodium chloride solution. The residue obtained upon removal of the solvent was heated under reflux for two hours with 3 g. of potassium hydroxide dissolved in 2 to 3 ml. of water and 60 ml. of diethylene glycol. After the solution had been diluted with water it was filtered and the filtrate was washed with ether. The aqueous solution was then acidified and extracted with ether and the extract was washed with water and dried over Drierite. When the residue obtained upon evaporation of the ether was dissolved in 20 ml. of dry benzene and allowed to stand for a few hours, colorless crystals precipitated. The product weighed 2.87 g. and melted at 171.5–174.5°. An additional 0.3 g. of crystalline material was obtained by diluting the mother liquor with petroleum ether. The pure compound obtained upon recrystallization from benzene melted at 192–194°. *Anal.* Calcd. for $C_{21}H_{30}O_3$: C, 76.3; H, 9.2; neut. equiv., 330. Found: C, 76.7; H, 9.3; neut. equiv. 331; $[\alpha]^{25}D$ +73° (1% in absolute ethanol).

6-Aminomethyldehydroabietic Acid (X).—This preparation was carried out according to the method of Delépine.[13] A solution of 5.0 g. of crude chloromethyldehydroabietic acid (VIII) and 1.7 g. of hexamethylenetetramine in 10 ml. of chloroform was heated under reflux for 20 minutes. The crystalline product obtained upon evaporating most of the chloroform and adding ether to the residue weighed 5.30 g. It was decomposed with dilute alcoholic hydrogen chloride in the usual manner and the reaction mixture was then evaporated to dryness. When the residue was extracted with 250 ml. of boiling water in several portions and the extract was cooled, 2.24 g. of colorless needles was obtained. A small second crop (0.47 g.) crystallized upon the addition of concentrated hydrochloric acid to the mother liquor.

When the total amine hydrochloride (2.71 g.) was dissolved in 15 ml. of pyridine and the solution was diluted with water, the free amine crystallized. Upon filtering and washing with water there was obtained 1.95 g. of product melting at 236–237°. The melting point rose to 239–240.5° after recrystallization from propanol-2 containing a little water. According to the analytical data it was monohydrate. *Anal.* Calcd. for $C_{21}H_{31}O_2N \cdot H_2O$: C, 72.7; H, 9.6; N, 4.0. Found: C, 72.8; H, 9.4; N (Kjeldahl), 4.0.

The acetate, obtained upon dilution of an acetic acid solution of the base with water, melted at 245–246°. *Anal.* Calcd. for $C_{21}H_{31}O_2N \cdot C_2H_4O_2$: C, 70.9; H, 9.1; N, 3.6. Found: C, 71.1; H, 9.3; N, 3.6.

Oxidation of Dehydroabietic Acid (I).—Fifty grams of dehydroabietic acid was partially dissolved in a solution of 10 g. of potassium hydroxide in 1 l. of water. A solution of 70 g. of potassium permanganate in 1500 ml. of water was added dropwise with stirring at approximately the rate at which it was reduced. The reaction mixture was then saturated with sulfur dioxide and the pale yellow solid was filtered off and washed with a large volume of water. The yield of crude material, λ_{max} 254 mμ, α 24.8, (α = specific absorption coefficient), was 41.5 g. (83% of the weight of dehydroabietic acid used).

If it is assumed as a rough approximation that the absorption at 254 mμ is due entirely to the keto acid XIII it may be calculated that the crude oxidation product contained 65% of this compound. On this basis, it is estimated that 52% of the dehydroabietic acid was converted to the keto acid.

In the above oxidation four atoms of oxygen per mole of dehydroabietic acid were available. When this oxygen : acid ratio was reduced to 3 : 1, the weight of the product was equal to that of the starting material but the specific absorption coefficient at 254 mμ fell to 21.6. When the ratio was increased to 5.5 : 1, the specific absorption coefficient at 254 mμ rose to 29.5, but only 66% of the weight of the starting material was recovered.

Isolation of Ketodehydroabietic Acid (XIII).—A solution of 20 g. of crude oxidized dehydroabietic acid (λ_{max} 254 mμ, α 24.8) in 200 ml. of absolute ethanol was heated under reflux with 20 g. of Girard Reagent T (trimethylacethydrazide ammonium chloride)[8] and 20 ml. of glacial acetic acid for one hour. After the addition of 200 ml. of ethylene glycol most of the ethanol was removed in vacuum. The residual solution was washed nine times with anhydrous ether to remove essentially all of the ether soluble material.[14] It was then treated at room temperature for one hour with a solution of 100 ml. of concentrated hydrochloric acid in 1200 ml. of water. The resulting precipitate was taken up in ether and the ether solution was washed and dried. After evaporation of the solvent the residue was converted in vacuum to a brittle froth which could be powdered and dried. The yield was 12 g.

A solution of 5 g. of this crude product in dilute methanol was seeded with crystals obtained by cooling a concentrated ether solution of the material and was further diluted with water over a period of several days. The large prisms which separated were filtered and washed with dilute methanol. The yield of product which melted at 156–161° was 3.22 g. The pure compound (2.66 g.) obtained upon recrystallization melted at 160–161.5°. *Anal.* Calcd. for $C_{20}H_{26}O_3$: C, 76.4; H, 8.3; neut. equiv., 314. Found: C, 76.5; H, 8.6; neut. equiv., 314.

Oxime of Ketodehydroabietic Acid.—One gram of the crude keto acid (XIII) isolated by means of Girard Reagent (above), was dissolved in 10 ml. of ethanol and the solution was heated under reflux for two hours with 1 g. of hydroxylamine hydrochloride and 5 ml. of pyridine. The resulting solution was diluted with water and extracted with ether and the ether extract was washed with dilute hydrochloric acid and water and dried over Drierite. Upon removal of the solvent there was obtained 0.9 g. of crude, crystalline product which was recrystallized from dilute methanol as long needles that decomposed at about 250°. *Anal.* Calcd. for $C_{20}H_{27}O_3N$: C, 72.9; H, 8.3; N, 4.3. Found: C, 73.1; H, 8.6; N, 4.4.

Wolff-Kishner Reduction of Ketodehydroabietic Acid (XIII).—This procedure is an adaptation of the method of Whitmore and collaborators.[15] A solution of 0.5 g. of pure ketodehydroabietic acid (XIII), and 0.5 ml. of 85% hydrazine hydrate in 8 ml. of absolute ethanol was heated under reflux for one hour in a water-bath. The hydrazone began to crystallize after about 15 minutes of heating. After the reaction mixture had been cooled to 0° the product was filtered off and washed with cold absolute ethanol. The yield was 0.45 g. of hydrazone which melted with decomposition at about 200°.

This hydrazone was reduced with 0.11 g. of sodium methoxide in 2.7 ml. of triethylene glycol. The reaction mixture was heated rapidly to 170° and the temperature was then gradually raised to 200° over a period of three-fourths hour. This temperature was maintained for one-half hour longer, by which time the evolution of gas had virtually ceased. After dilution with water the solution was acidified and the precipitate was filtered off. The crude dehydroabietic acid was dissolved in low boiling petroleum ether and the solu-

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[13] M. Delépine, *Bull. soc. chim.*, [3] **17**, 290 (1897).

[14] This modification[8] of the general procedure was followed because of the acidic nature of the product.

[15] F. C. Whitmore, *et al.*, THIS JOURNAL, **67**, 2059 (1945).

tion was chilled and filtered to remove a dark amorphous impurity. After removal of the solvent the acid was dissolved in ethanol, treated with Norite and crystallized by the gradual addition of water. The product (0.23 g., 48%), melted at 165–168°. Further recrystallization yielded 0.16 g. of material with a melting point of 169–170°. This product did not depress the melting point of an authentic sample of dehydroabietic acid (I).

The methyl ester, prepared with dimethyl sulfate, melted at 62–63°. A mixed melting point with an authentic sample of methyl dehydroabietate showed no depression.

Oxidation of Chloromethyldehydroabietic Acid (VIII).—A sample (4.2 g.) of crude chloromethyldehydroabietic acid, containing 8.2% of chlorine, was partially dissolved in a solution of 0.4 g. of potassium hydroxide in 100 ml. of water. A solution of 4.7 g. of potassium permanganate and 1 g. of potassium hydroxide in 100 ml. of water was slowly added with stirring over a period of five hours. Saturation of the reaction mixture with sulfur dioxide produced a precipitate which was filtered off, washed with water and dissolved in ether. The ether solution was extracted with dilute sodium bicarbonate and the aqueous extract was acidified. Upon the addition of ether to this extract the product crystallized and was filtered off. The first crop weighed 1.82 g.; an additional 0.10 g. was obtained upon concentrating the ether layer to a small volume. The neutral equivalent of the crude product was 182. It did not melt below 280°. It was purified by recrystallization from ethanol and water. *Anal.* Calcd. for $C_{21}H_{26}O_5$: C, 70.4; H, 7.3; neut. equiv., 179. Found: C, 70.6; H, 7.5; neut. equiv., 179; $[\alpha]^{25}\text{D}$ +38° (1% in absolute ethanol).

The dimethyl ester (XV) prepared by treating the acid with diazomethane and recrystallizing from methanol and water, melted at 94–95°. *Anal.* Calcd. for $C_{23}H_{30}O_5$: C, 71.5; H, 7.8. Found: C, 71.7; H, 8.0.

The oxime was prepared from the above dimethyl ester by heating it under reflux with an equal weight of hydroxylamine hydrochloride in an alcohol solution containing excess pyridine. After recrystallization from dilute methanol the product melted at 192–194°. *Anal.* Calcd. for $C_{23}H_{31}O_5N$: C, 68.8; H, 7.8; N, 3.5. Found: C, 69.0; H, 7.9; N, 3.6.

Oxidation of 6-Carboxydehydroabietic Acid (III).—To a solution of 1 g. of this acid (III) in 40 ml. of water containing 0.38 g. of potassium hydroxide there was added with stirring a solution of 0.94 g. of potassium permanganate in 20 ml. of water over a period of three hours. The reaction mixture was saturated with sulfur dioxide and the precipitate was filtered off and washed with water. It was then dissolved in sodium bicarbonate solution and treated with Norite. Upon acidification there was obtained 0.75 g. of crude acid ($[\alpha]^{25}\text{D}$ +31°, 1% in absolute ethanol). The product was recrystallized from ethanol and water.

Treatment of this acid with diazomethane and recrystallization from dilute methanol gave the dimethyl ester (XV) which melted at 94–95°. A mixture of this ester with the dimethyl ester obtained from oxidized chloromethyldehydroabietic acid (above) melted at the same temperatures.

Ultraviolet Absorption Spectra.—The absorption spectra were obtained from measurements made with a Beckman model DU quartz spectrophotometer. The solvent for dehydroabietic acid was ethanol and the concentration was 500 mg. per l.; that for the other compounds was methanol and the concentrations were approximately 20 mg. per l.

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Ketene Acetals. XXV. Diphenylketene Dimethylacetal

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The preparation of diphenylketene dimethylacetal (IV) by the dehydrochlorination of diphenylchloroacetaldehyde dimethylacetal (III) is described. This is the principal reaction between III and potassium *t*-butoxide in dioxane, but in *t*-butyl alcohol this base causes nearly an equal amount of replacement of the halogen to form the *t*-butoxyacetal (V). Similar reactions occur between III and sodium pinacolate in pinacol solution. IV shows the expected reactions with water, methanol, benzyl bromide and bromine; it is, however, singularly unreactive toward acyl chlorides. IV undergoes a novel reaction with potassium *t*-butoxide to yield the potassium enolate of methyl diphenylacetate and methyl *t*-butyl ether. Diphenylhaloacetaldehyde acetals (II, IX and X) are found to undergo a novel thermal rearrangement into the corresponding diphenylacetic ester and alkyl halide. An attempt to prepare diphenylketene diethylacetal from IX was unsuccessful because of the interference of the halogen replacement reaction and the decomposition of the ketene acetal to the potassium enolate of ethyl diphenylacetate.

Diphenylketene dimethylacetal (IV) has been prepared by the dehydrochlorination of diphenylchloroacetaldehyde dimethylacetal (III), obtained from methyl dimethoxyacetate (I) *via* the sequence of reactions shown below. The dehydrochlorination of III with potassium *t*-butoxide in *t*-butyl alcohol, which has been used effectively for the dehydrohalogenation of a variety of haloacetals to the corresponding ketene acetals,[3] was accompanied by a concurrent replacement reaction that yielded the *t*-butoxyacetal (V). This compound and the ketene acetal (IV) were formed in 39 and 47% yields, respectively, as determined from the refractive index of a distilled mixture of these products. This mixture was partially separated by fractional distillation after a portion (*ca.* 65%) of IV, m.p. 66–68°, crystallized from the mixture on cooling. Similarly the reaction of III with sodium pinacolate in pinacol gave the ketene acetal (IV) and a compound corresponding to the pinacoloxyacetal (VI); because of the greater difference in boiling points of IV and VI, they were readily separated by fractionation in yields of 38 and 42%, respectively.

The most satisfactory procedure for the dehydrochlorination of III utilized dry potassium *t*-butoxide in refluxing dioxane. In this reaction none of the *t*-butoxyacetal (V) was formed and the pure ketene acetal (IV) was obtained readily in 50% yield. The use of the higher boiling dibutyl ether instead of dioxane gave only a 30% yield of IV, the potassium enolate of methyl diphenylacetate (see below for the formation of this product), and a considerable amount of tar.

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