tenths mole), both in water, were added to 7.9 g. of pyridine (one-tenth mole) in the cold; a red color appears at once, and after a few moments, a red-violet solid separates. The yield is nearly quantitative. The same reaction takes place in ether. The product was recrystallized from alcohol. Suspended in alcohol with the proper acidity provided, neither the crude product nor the purified material reacted with nitrous acid.

The same reaction was performed with β-hydroxypyridine, bromocyanogen and aniline in ether. The product was a bluish-black crystal mass, which did not react with nitrous acid. Bromocyanogen was prepared by the method of of Scholl[14] with excellent results, provided the potassium cyanide solution was added drop by drop, to the bromide covered with a little water, and well-cooled in an ice-bath.

**1-Phenyl-3-hydroxy Pyridinium Bromide and Chloride.**—By refluxing Schiff base with glacial acetic acid for twelve hours, a black tarry material was formed which after extraction with acetone was further extracted with hot water, in order to obtain the pyridinium salt. After recrystallization from alcohol, the proper melting points were recorded. Boiling Schiff base with alcohol instead of acetic acid gave a much smaller yield, and the boiling had to be continued for forty-eight hours.

## Summary

The violet substance known as Schiff base has been shown to possess two free amino groups; therefore the formula originally suggested by Schiff representing it as a derivative of diphenylfurylmethane, should be favored over that proposed by Zincke, an open chain compound with unsaturation. The main support for this latter formula is the formation of 1-phenyl-3-hydroxypyridinium bromide or chloride, by glacial acetic acid treatment, but a reasonable explanation for its formation from the dianilinofurylmethane structure is given, so that this possible objection to the original formula of Schiff is removed.

BUFFALO, NEW YORK RECEIVED MARCH 28, 1941

[14] Scholl, *Ber.*, **29**, 1822 (1896).

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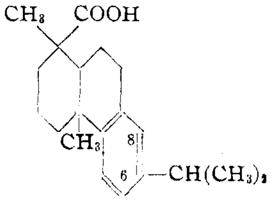
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# Substitution Reactions of Dehydroabietic Acid. II

BY WILLIAM P. CAMPBELL AND MORLEY MORGANA

Dehydroabietic acid[1] (I) is a readily available hydrophenanthrene derivative which offers promise of becoming a useful starting material for the synthesis of industrially or physiologically important products, by the introduction of suitable substituents into the aromatic ring and by alteration of the carboxyl group. It was with this ultimate goal in mind that this series of investigations was undertaken. One derivative of the type indicated, 6-hydroxydehydroabietinol (II),[2,2a] has been found to possess considerable oestrogenic activity.

Of the limited number of substitution products of dehydroabietic acid that have been reported, only those derived from the 6- and 8-acetyl derivatives[1b,2] are of known structure. No positive evidence has been brought forward concerning the location of the substituents in sulfodehydroabietic acid (III)[1b,3] or in the dinitro (VII),[1,4] or the nitro-sulfo (XI)[5] derivatives. In this work the position of the sulfonic acid group in these compounds is established and one of the nitro groups is definitely located. In addition, new derivatives of dehydroabietic acid are reported together with a new route to the important 6-amino and 6-hydroxy compounds.



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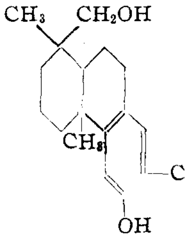

II

The sulfonic acid group of sulfodehydroabietic

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[1] (a) Fieser and Campbell, THIS JOURNAL, **60**, 159 (1938); (b) **60**, 2631 (1938).

[2] Fieser and Campbell, *ibid.*, **61**, 2528 (1939).

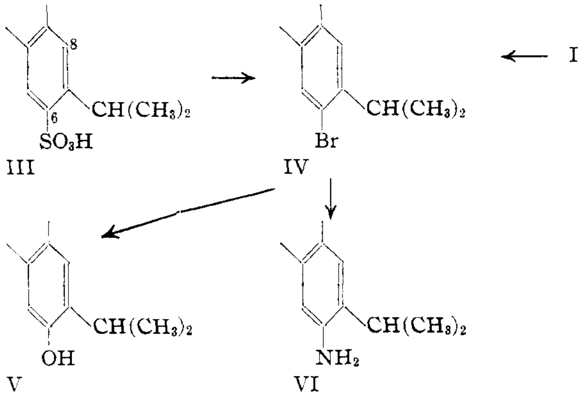
[2a] Another derivative, 6-dimethylaminodehydroabietinol methyl ether hydrochloride,[2] has been tested for analgesic activity by Dr. Nathan B. Eddy through the courtesy of Dr. Lyndon F. Small. His report follows: "Toxicity—Only two dose levels were given to mice, 300 and 500 mg. per kg. Only mild depression was seen, without apparent change in reflex activity or coördination, and with little muscular weakness even with the larger dose. It is presumed that the fatal dose would lie well above 500 mg. per kg. Analgesic effect —Doses of 100 and 200 mg. per kg. were administered orally to cats. Very slight depression followed the larger dose but there was no analgesic effect. The substance was not emetic in the doses administered." Thus the compound is relatively inactive in all respects.

[3] Fanica, *Bull. inst. pin*, **44**, 151 (1933); Hasselstrom, *et al.*, THIS JOURNAL, **60**, 1267, 2340 (1938).

[4] Johansson, *Arkiv. Kemi. Min. Geol.*, **6**, No. 19 (1917).

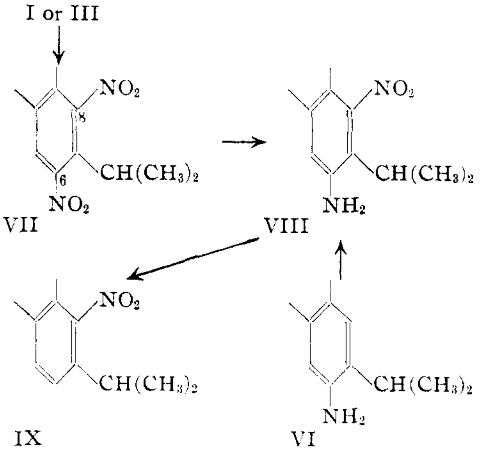
[5] Hasselstrom and Hopkins, THIS JOURNAL, **63**, 421 (1941).

acid (III) is replaced by bromine in aqueous solution in 92% yield. The conversion of the resulting bromo acid (IV) to the known 6-hydroxy (V) and 6-amino (VI) derivatives[2] identifies both the sulfo and bromo acids as 6-derivatives. The 6-hydroxy derivative was prepared by heating the 6-bromo acid in a copper container in an autoclave with aqueous sodium hydroxide at 300°. Similarly, aqueous ammonia at 200° replaced the bromine by an amino group. In view of these reactions it is surprising that treatment of 6-sulfodehydroabietic acid with aqueous sodium hydroxide at 300° apparently brings about deep-seated alteration of the molecule.[1b] Dehydroabietic acid has been subjected to this treatment without appreciable alteration, and now it is apparent that the 6-hydroxy acid, if it were formed from the sulfo acid, possesses sufficient stability to withstand the high temperatures.



The 6-bromo acid was also obtained by bromination of dehydroabietic acid in carbon tetrachloride solution. The yield in these preliminary experiments was low and attempts to improve it were abandoned when the preparation from the sulfo acid was discovered. The bromo acid could not be obtained in pure form even after many crystallizations as the acid and as the ammonium salt, and neutral equivalents of various fractions suggested contamination with the starting material. However, esterification of various fractions, even those of low purity, yielded pure methyl 6-bromodehydroabietate quite readily. Although this reaction has no preparative value, it shows that the orientation in bromination is the same as in other substitutions.

Although no direct evidence concerning the location of the nitro groups in dinitrodehydroabietic acid (VII) has been reported, the known facts strongly indicate the 6- and 8-positions. It has been pointed out[1b] that the easy introduction of two nitro groups into the molecule suggests that these groups enter in meta positions. This view is supported by the fact that even under very mild conditions the nitration of dehydroabietic acid cannot be stopped at the mononitro stage. Since the only meta positions available are 6 and 8, the compound has been represented as this derivative.[1] Now that the sulfo group of III has been located at position 6, the replacement of this group by a nitro group in the formation of the dinitro compound from the 6-sulfonic acid provides further evidence that one of the nitro groups is in the 6-position. The following reactions prove that this is the case. Methyl dinitrodehydroabietate was reduced by ammonium sulfide in excellent yield to an amino-nitro ester (VIII). It was assumed that the less hindered 6-nitro group was reduced. The same amino-nitro compound was prepared by the nitration of 6-aminodehydroabietic acid using molar quantities of nitric acid in sulfuric acid solution, followed by esterification with diazomethane. The amino group of the amino-nitro ester (VIII) is, therefore, in the 6-position, as is one of the nitro groups in the dinitro derivative. With this fact established, there can be little doubt that the other nitro group is in the 8-(meta) position.

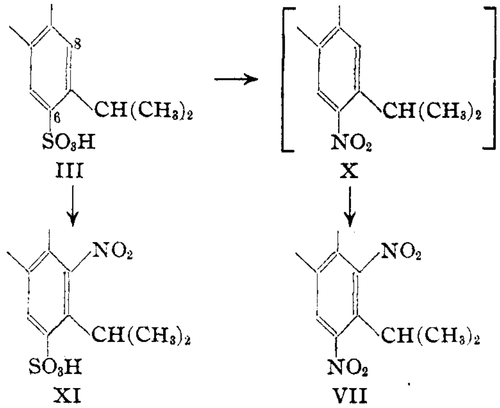


The substitution products of dehydroabietic acid of most interest in connection with the preparation of compounds of possible physiological activity are the 6-amino and the 6-hydroxy derivatives. These have been prepared[2] by a rather long series of reactions by way of 6-acetyldehydroabietic acid. Although, in general, the reactions in this series can be carried out with good yields, the preparation of quantities of the compounds is a tedious process. The conversion of 6-bromodehydroabietic acid, prepared from the sulfonic acid, into the 6-hydroxy and 6-amino derivatives as described above, makes these substances readily available in quantity. The over-all yields of the hydroxy and amino derivatives from the sulfonic acid are 40 and 38%, respectively. Only two steps are required and the method is rapid and easily adaptable to large scale work. The yields by the older method differ only slightly from those above (32 and 47%, respectively), but five to six steps are necessary.

Of equal interest in this connection would be the 8-amino and 8-hydroxy derivatives, and it was partly for this reason that we undertook to study some reactions which would make these substances available. The only 8-derivative of dehydroabietic acid which has been reported is the 8-acetyl compound.[2] This substance is formed in very small amounts along with the 6-isomer in the Friedel and Crafts reaction. Difficulties involved in isolation and the highly hindered character of the acetyl group render this compound unsuitable for further degradation. By replacement of the amino group of methyl 6-amino-8-nitrodehydroabietate (VIII) by hydrogen through the diazonium salt, we have been able to prepare the 8-nitro derivative (IX) in 40% yield. We plan to convert this compound into the corresponding amino and hydroxy derivatives.

It occurred to us that the nitrosulfodehydroabietic acid of Hasselstrom and Hopkins,[5,6] which we can now write as the 6-sulfo-8-nitro compound (XI), might offer a more convenient route to the 8-nitro derivative, but several attempts to accomplish the hydrolysis of the sulfonic acid group have failed. When heated in 55 to 60% sulfuric acid at 135° for twenty-four hours, part of the material was not attacked and the water insoluble part was a black tarry substance. Variations in temperature or time produced a corresponding variation in the quantity of the tarry material. In addition, the sulfonic acid group of the 6-sulfo-8-nitro compound could not be replaced by bromine under the conditions which were used for 6-sulfodehydroabietic acid.

We have obtained the nitro-sulfo derivative by nitrating 6-sulfodehydroabietic acid under different conditions and our experiments give some information concerning the course of the reaction. When a solution of the 6-sulfo acid in concentrated sulfuric acid was treated with a molar quantity of concentrated nitric acid, the nitro-sulfo acid was formed in good yield along with 3% of water-insoluble material which was identified as the 6,8-dinitro derivative. When the nitration was run in 2 to 1 sulfuric–nitric acid mixture, 22% of the dinitro acid was formed. Treatment of the 6-sulfo-8-nitro acid with the 2 to 1 mixed acids produced only a trace of water-insoluble material.



Based on these reactions, the following conclusions seem valid. The two products are formed by independent reactions which take place simultaneously. The substitution reaction, leading to the nitro-sulfo acid (XI), is more rapid and the 8-nitro group in this product prevents replacement of the sulfonic acid group. This deactivating influence is in line with the observed stability of this sulfonic acid group to hydrolysis and to replacement by bromine. The dinitro acid (VII) is formed by way of the intermediate 6-nitro derivative (X), and this relatively slow reaction is followed by a rapid nitration to VII. The replacement reaction (III → X) apparently does not occur to an appreciable extent when fuming nitric acid alone is used, since Hasselstrom and Hopkins[5] reported the formation of only a minute amount of water-insoluble material with this reagent.

In regard to the preparation of dehydroabietic acid and the 6-sulfo derivative, some difficulties, not previously encountered, should be reported. It was stated in an earlier publication[2] that

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(6) These authors apparently have misinterpreted the aims of nitration experiments of Fieser and Campbell[1b] to which they refer. The purpose of these tests was to determine whether the sulfonic acid group could be replaced, forming the 6-nitro derivative. Hence only the water-insoluble products were of interest at that time.

Steele's acid,[7] which had been further purified by one crystallization as the sodium salt, was sufficiently pure for this process. This was observed when using "commercial abietic acid" supplied by the Hercules Powder Company[8] as the starting material. Since then, we have attempted to repeat this using different batches of WW rosin and "commercial abietic acid" from other sources and it was found necessary to crystallize the sodium salt a total of three or four times. Without this additional purification, the "pyro acid" did not crystallize readily and the yield of sulfonic acid was very low. Using the more highly purified starting material, and a different method of isolating the sulfonic acid, this substance was obtained in improved yields as the trihydrate.

## Experimental Part[9]

**The Preparation of 6-Sulfodehydroabietic Acid (III).**—This preparation was carried out as previously described[1] with the following modifications. The starting material was Steele's acid[7] which was further purified by three crystallizations as sodium tetraabietate. After this treatment both the sodium salt and the regenerated acid gave colorless solutions in alcohol. The crude sulfonic acid was dissolved in hot water and the resulting cloudy solution was filtered through thin layers of Norit with suction until clear. Concentrated hydrochloric acid precipitated the sulfonic acid from this solution. The product, after air-drying at 50°, was obtained as the trihydrate.[3] When this material is immersed in a melting point bath at 215°, it melts with the evolution of water, immediately resolidifies, and then decomposes at 227°. If the sample is immersed at 100°, no apparent change takes place until decomposition occurs at 230°. The yield from "pyroabietic acid" was 78%.

*Anal.* Calcd. for $C_{20}H_{28}O_5S \cdot 3H_2O$: neut. equiv., 218. Found: neut. equiv., 218.

**6-Bromodehydroabietic Acid (IV).** (a) **From 6-Sulfodehydroabietic Acid.**—To a stirred solution of 45 g. of 6-sulfodehydroabietic acid trihydrate in 1 liter of water at steam-bath temperature, was added a solution of 29 g. of bromine (50% excess) and 40 g. of sodium bromide in 1 liter of water, over a three-hour period. The heavy white precipitate which formed during this time was separated by filtration, washed thoroughly with hot water and dried. The yield was 36 g. (92%) of nearly pure 6-bromo acid, m. p. 198–200°. One crystallization from aqueous ethanol gave pure material, m. p. 200–202°, $[\alpha]^{25}D$ +81° (0.80 g. per 100 cc. of ethanol).

*Anal.*[9a] Calcd. for $C_{20}H_{27}O_2Br$: C, 63.32; H, 7.18; neut. equiv., 379. Found: C, 63.07; H, 7.26; neut. equiv., 375.

No starting material could be precipitated from the aqueous filtrate of the reaction mixture by concentrated hydrochloric acid. Pure bromine may be used in place of the solution of bromine in aqueous sodium bromide with equally good results.

The **methyl ester** of this compound was prepared by treating the acid with excess diazomethane in ether solution. After crystallization from ether–hexane the product melted at 140.5–141°, $[\alpha]^{25}D$ +71° (0.93 g. per 100 cc. of acetone).

*Anal.* Calcd. for $C_{21}H_{29}O_2Br$: C, 64.10; H, 7.43. Found: C, 64.20; H, 7.64.

(b) **From Dehydroabietic Acid.**—In a typical experiment dehydroabietic acid was treated with 25% excess bromine in carbon tetrachloride solution at 60° for twenty-eight hours. Crystallization of the product of this reaction from alcohol, either as the free acid or the ammonium salt, gave fractions of acid with melting ranges from 185–190° to 192–198° and neutral equivalents from 354 to 360 (calcd.: 379). However, 1.8 g. of a mixture of various fractions of this kind, on treatment with diazomethane in ether gave, after one crystallization, 1.1 g. of pure methyl ester, m. p. 140.5–141°.

**Methyl 6-Hydroxydehydroabietate (V).**—A mixture of 5 g. of 6-bromodehydroabietic acid and 150 cc. of 12% aqueous sodium hydroxide was heated in a copper can, in an autoclave, under nitrogen at 290° for fifteen hours. After cooling, 250 cc. of water was added, the solution was filtered, and the product was precipitated from the filtrate with hydrochloric acid. Treatment of this solid in ether solution with excess diazomethane and two crystallizations from ether–hexane gave 1.44 g. (27%) of pure hydroxy ester, m. p. 158–161.5°. This melting point is somewhat higher than that previously reported[2]; however, samples melting at this temperature also have been obtained by the earlier method. A mixed melting point determination proved the identity of the ester prepared above.

Subsequent runs by others in this laboratory, under the same conditions but on a considerably larger scale, have given a 44% yield of the ester of nearly the same purity.

Lower yields resulted from the use of potassium instead of sodium hydroxide or from operation at a lower temperature.

**6-Aminodehydroabietic Acid (VI).**—In an autoclave reaction conducted as described above, 10.3 g. of the 6-bromo acid was heated with 200 cc. of concentrated ammonium hydroxide containing 2 g. of cuprous bromide for twelve hours at 200°. The cooled reaction mixture was washed through a filter with water. A neutral, water-insoluble product was extracted from the residue on the filter by alcohol. This material, which has not been investigated further, may contain amides of the bromo or amino acids. The deep blue ammoniacal filtrate was acidified with acetic acid and the resulting precipitate was removed by filtration and washed with water. This product was taken up in ether, extracted into 1% sodium hydroxide solution, and again precipitated with acetic acid. To an ether solution of the dried precipitate was added an equal volume of a saturated ethereal solution of hydrogen chloride, when 5.65 g. (59%) of crystalline hydrochloride was precipitated. The free amino acid was regenerated by dissolving the hydrochloride in 300 cc. of

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(7) Steele, THIS JOURNAL, **44**, 1333 (1922).

(8) We wish to thank Dr. Emil Ott of this company for a generous supply of this material.

(9) All melting points are corrected.

(9a) This analysis by Miss Eleanor Werble.

ethanol containing 2 g. of potassium hydroxide, acidifying with acetic acid, and precipitating by the addition of water. One crystallization (Norit) from 60% ethanol gave 3.57 g. (42%) of nearly colorless 6-amino acid, m. p. 211–214°. A mixed melting point determination confirmed the identity of this substance.

**Methyl 6-Amino-8-nitrodehydroabietate (VIII).**—A suspension of 16 g. of methyl 6,8-dinitrodehydroabietate in 3 liters of methanol and 25 cc. of concentrated ammonium hydroxide was refluxed for twenty-six hours. During this period a slow stream of hydrogen sulfide was passed through the mixture and 400 cc. more of concentrated ammonium hydroxide was added dropwise. After about nine hours the dinitro ester had dissolved completely and the initial deep green color had changed to dark red. At the end of the twenty-six hour period about three-quarters of the methanol was evaporated and 1500 cc. of water was added. The crystalline precipitate, air-dried at 50°, weighed 19.5 g. and probably contained considerable sulfur (theoretical weight, 14.8 g.). A suspension of this material in 1 liter of ether was saturated with dry hydrogen chloride. The suspended solid changed in appearance during this treatment and on filtration 16.7 g. of material (m. p. 247–248.5°) which is at least partly hydrochloride was obtained. Recrystallization from 95% ethanol gave, in two crops, 13.5 g. (91%) of the free amino-nitro ester in a pure condition, m. p. 239–242°, $[\alpha]^{25}D$ +105° (0.82 g. per 100 cc. of acetone). Further crystallization did not change the melting point.

*Anal.* Calcd. for $C_{21}H_{30}O_4N_2$: C, 67.33; H, 8.07. Found: C, 67.35; H, 7.91.

In subsequent runs the volume of methanol required for this preparation was decreased by using a solution of ammonia in methanol instead of aqueous ammonia.

**Methyl 6-Diacetylamino-8-nitrodehydroabietate.**—A solution of 1.0 g. of the amino-nitro ester in 10 cc. of acetic anhydride was heated at the boiling point for ten minutes. After cooling, the mixture was warmed on the steam-bath for ten minutes more with 50 cc. of water and the white crystalline precipitate which separated was collected and washed with water on a filter; yield 1.1 g., m. p. 200–202°. Recrystallization from methanol gave colorless prisms, m. p. 203.5–206°, $[\alpha]^{25}D$ +97° (1.0 g. per 100 cc. of acetone).

*Anal.* Calcd. for $C_{25}H_{34}O_6N_2$: C, 65.48; H, 7.47. Found: C, 65.67; H, 7.41.

**6-Amino-8-nitrodehydroabietic Acid (VIII).**—This substance was obtained in a preliminary experiment on the reduction of the 6-nitro group which was run on the dinitro acid. The method used was similar to that of Murray and Waters.[10] To a solution of 13 g. of the dinitro acid in 500 cc. of concentrated ammonium hydroxide and 500 cc. of ethanol was added a solution of 30 g. of $Na_2S \cdot 9H_2O$ and 13.5 g. of ammonium chloride in 150 cc. of water. After refluxing for nineteen hours the solution was acidified with dilute hydrochloric acid, most of the ethanol was removed by distillation and 500 cc. of water was added. The precipitate (12.3 g.) was dissolved in ether and, after filtering to remove a small amount of insoluble material, dry hydrogen chloride was passed into the solution. The precipitated hydrochloride (2.95 g., 22%) was dissolved in 200 cc. of boiling ethanol with some difficulty and, on concentrating the solution and cooling, the free amino-nitro acid (1.81 g.) crystallized, m. p. 281.5–282° dec. One recrystallization from aqueous ethanol gave 1.34 g. (11%) of pure acid which melted constantly at 285.5–286° dec., $[\alpha]^{25}D$ +117° (0.97 g. per 100 cc. of acetone).

*Anal.*[9a] Calcd. for $C_{20}H_{28}O_4N_2$: C, 66.65; H, 7.83. Found: C, 66.99; H, 7.70.

From the ether filtrate there was obtained 7 g. of starting material.

Esterification of a sample of this material with diazomethane in ether solution gave the same methyl ester (m. p. 241–243.5°) that was obtained by reduction of the dinitro ester.

**The Nitration of 6-Aminodehydroabietic Acid.**—To a solution prepared by dissolving 0.2 g. of 6-aminodehydroabietic acid in 6 cc. of concentrated sulfuric acid in an ice–salt-bath was added, with stirring, 0.04 cc. of concentrated nitric acid. After thirty minutes, the solution was poured into 75 cc. of ice and water and the yellow precipitate was collected on a filter and washed with water. Crystallization from aqueous ethanol gave 0.14 g. of yellow needles, m. p. 277–279° dec. Part of this (0.09 g.) was recrystallized from aqueous ethanol and 0.05 g. of 6-amino-8-nitrodehydroabietic acid, m. p. 282.5–283° dec., was obtained. Mixed with a sample of this acid prepared above, the melting point was the same.

The remainder of the first crop of material (0.05 g.) was treated with excess diazomethane and 0.03 g. of the methyl ester, m. p. 241–243°, was obtained. A mixed melting point with methyl 6-amino-8-nitrodehydroabietate gave no depression.

**Methyl 8-Nitrodehydroabietate (IX).**—The method described by Schoutissen[11] for the diazotization of weakly basic amines was followed. Methyl 6-amino-8-nitrodehydroabietate (2.7 g.) was dissolved in 25 cc. of concentrated sulfuric acid and to this stirred solution was added a solution of 0.7 g. of sodium nitrite in 15 cc. of concentrated sulfuric acid. Eighty cc. of phosphoric acid (sp. gr. 1.7) was added dropwise while the temperature was maintained at 0°. The addition required one hour, and after stirring for twenty minutes more the yellow solution was poured into 500 g. of ice and water. The fine white crystalline diazonium salt which precipitated after about five minutes was separated by filtration and suspended in 150 cc. of ethanol containing about 20 g. of powdered zinc. The diazonium salt dissolved at room temperature with the evolution of nitrogen and after one and one-half hours the mixture was filtered. After treating the filtrate with Norit and concentrating to about 20 cc., 0.37 g. of colorless plates, m. p. 191–193°, separated. By extraction of the zinc residue with ether and replacing the ether with hexane, 0.67 g. more of the product was obtained as needles, m. p. 191–193.5°. The total yield amounts to 40%. Recrystallization from aqueous ethanol gave pure material melting at 194–195°, $[\alpha]^{25}D$ +29° (0.70 g. per 100 cc. of acetone).

*Anal.* Calcd. for $C_{21}H_{29}O_4N$: C, 70.17; H, 8.13. Found: C, 69.94; H, 8.10.

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[10] Murray and Waters, This Journal, 60, 2818 (1938)

[11] Schoutissen, *ibid.*, 55, 4531 (1933)

In subsequent runs the yield was the same when zinc powder was omitted. Washing the diazonium salt on the filter with water dissolves part of it. If the wash water is run into the acidic filtrate, the salt crystallizes again in long white needles.

Nitration of this product (0.1 g.) with sulfuric–nitric acid mixture (3:2) at 0° gave methyl 6,8-dinitrodehydroabietate (0.05 g.), m. p. 185.5–188° after one crystallization from acetone–methanol. Mixed with pure dinitro ester the melting point was 187–188.5°.

**Nitration Experiments on the Sulfonic Acids.**—(a) To a solution of 4.35 g. of sulfonic acid trihydrate in 15 cc. of concentrated sulfuric acid, was added 0.65 cc. of concentrated nitric acid at ice-salt temperature. After stirring for fifteen minutes, the mixture was poured into 75 cc. of ice and water and the gelatinous precipitate was filtered and washed with a mixture of 35 cc. of concentrated hydrochloric acid and 70 cc. of water. Air-dried at 50° overnight, the product weighed 4.7 g. (calcd. for anhydrous sulfo-nitro acid, 4.25 g.). This product was boiled with 500 cc. of water and on filtration gave 0.12 g. (3%) of water insoluble material. By evaporation of the filtrate to dryness, 4.6 g. of water-soluble material was recovered.

The water-insoluble part was identified as 6,8-dinitrodehydroabietic acid by conversion to the methyl ester with diazomethane. There was obtained 0.08 g. which melted at 187.5–188°. Mixed with an authentic sample, the melting point was 188–188.5°.

One gram of the water-soluble part was dissolved in a few cc. of methanol and treated with excess diazomethane in ether. During this reaction the ester, which is only slightly soluble in ether, separated as a fine white crystalline precipitate, 0.65 g., m. p. 238.5–240°. A second crop of 0.15 g., m. p. 235–236.5°, was obtained on concentrating the ether solution, bringing the total yield to 81%. One crystallization from acetone gave pure dimethyl ester, m. p. 243.5–244°. The melting point of a mixture with the dimethyl ester of the sulfo-nitro acid of Hasselstrom and Hopkins[5] was the same.

(b) One gram of the 6-sulfo acid trihydrate was stirred into a mixture of 4 cc. of concentrated sulfuric acid and 2 cc. of concentrated nitric acid with cooling in an ice–salt-bath. After twenty minutes the mixture was poured into 30 to 40 cc. of ice and water, and worked up as above. The water-insoluble material weighed 0.2 g. (22%) and gave 0.17 g. of methyl 6,8-dinitrodehydroabietate, m. p. 185–186.5°, which melted at 187–188° when mixed with a known sample.

(c) Treatment of 1.0 g. of the sulfo-nitro acid prepared in (a) with mixed acids as described in part (b) gave only a trace (about 0.02 g.) of water-insoluble material.

## Summary

1. The sulfonic acid group in sulfodehydroabietic acid and in the nitro-sulfo derivative has been shown to be located at position 6. The same position is occupied by one of the nitro groups of the dinitro derivative.

2. The 6-amino and 6-hydroxy derivatives of dehydroabietic acid have been prepared by a new method which makes these substances easily available in quantity.

3. The 8-nitro derivative, which is to be used for the preparation of the corresponding hydroxy and amino compounds, has been prepared.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 12, 1941

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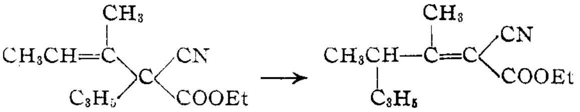
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

# The Rearrangement of Allyl Groups in Three-Carbon Systems. I.[1]

BY ARTHUR C. COPE,[2] KATHRYN E. HOYLE AND DOROTHEA HEYL

It was reported recently that ethyl (1-methylpropenyl)-allylcyanoacetate rearranged on heating to ethyl (1,2-dimethyl-4-pentenylidene)-cyanoacetate.[3]



This $\alpha,\gamma$-shift of an allyl group in a three-carbon system involves structural changes similar to those occurring in the familiar Claisen rearrangement of allyl phenol, enol and vinyl ethers. This paper describes work undertaken to determine whether the rearrangement is general for appropriately substituted three-carbon systems, just as the Claisen rearrangement is general for the $\rangle C{=}\underset{|}{C}{-}OC_3H_5$ system.

By alkylation methods previously described,[4] six cyanoacetic esters, four malonic esters and two malononitriles were prepared, each disubstituted by an alkyl vinyl and an allyl group. All of these compounds rearranged on heating, and in all but two cases the rearrangements were relatively free from side reactions, so that pure products could be isolated. It was considered important to prove

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[1] Supported by a grant from the Penrose Fund of the American Philosophical Society.

[2] A. C. C. is indebted to the John Simon Guggenheim Memorial Foundation for the award of a fellowship in the general field of this investigation.

[3] Cope and Hardy, THIS JOURNAL, 62, 441 (1940).

[4] Cope and Hoyle, *ibid.*, 63, 733 (1941), and preceding papers.