

[CONTRIBUTION FROM THE LABORATORY OF THE TECHNICAL UNIVERSITY OF FINLAND]

A CONTRIBUTION TO THE CHEMISTRY OF DIHYDRORETENE¹

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Introduction and Historical

Retene is a hydrocarbon, 1-methyl-7-isopropylphenanthrene, derived from pine tar. The hydrogenated derivatives of retene are of interest especially because of their relationship to resin acids and in view of their occurrence with retene in pine tar and pine oils.

Dihydroretene may be obtained as a well-characterized, crystalline material by carefully reducing retene with sodium and amyl alcohol. Virtanen,² who first isolated dihydroretene by this method, found that the compound, unlike retene, formed no picrate and that it yielded retenequinone on chromic acid oxidation.

It is well known that phenanthrene is more closely related to diphenyl in its chemical behavior than to naphthalene. This property is clearly evident in a series of reactions of phenanthrene in which the double bond of the 9,10 position, the "bridge," appears almost olefinic in nature. It is to be expected that the middle ring of the retene molecule should have the same character as that of phenanthrene. A ring system obtained by saturating the "bridge" double bond of retene should in many respects bear a close relationship to the mother substance, although it is to be expected that the aromatic character of the other two benzene nuclei should be enhanced.

Monosubstitution derivatives of retene have been prepared by halogenation, carboxylation and sulfonation.³ Of these, the last mentioned are the best characterized. Komppa and Wahlforss⁴ isolated two monosulfonic acids and from them prepared a series of well-characterized derivatives. These sulfonic acids, designated as A-retenesulfonic acid and B-retenesulfonic acid, are colorless, crystalline substances free of water of crystallization and possess sharp melting points.⁵ In view of these

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² Virtanen, *Ber.*, **53**, 1880 (1920).

³ Additional derivatives of retene have recently been reported by Bogert and Hasselström, *THIS JOURNAL*, **53**, 3462 (1931), and by Fieser and Young, *ibid.*, **53**, 4120 (1931). (Abstractors' note.)

⁴ Komppa and Wahlforss, *ibid.*, **52**, 5009 (1930).

⁵ Fieser and Young suggest that the A- and B-substituents occupy the 2- and 6-positions, respectively, in retene. In this connection they state: "While no promising

circumstances it seemed desirable to study similar reactions of dihydroretene.

Results and Discussion

The sulfonation of dihydroretene gave, in good yields, two monosulfonic acids. Sulfonation at 66° resulted in the formation of a monosulfonic acid which was characterized by its difficultly soluble alkali salts. The acid, purified by means of its barium salt, when recrystallized from ether melted at $147-148^{\circ}$. Sulfonation at 200° resulted in the formation of a second monosulfonic acid which, when regenerated from its ethyl ester and recrystallized from benzene, melted at $106-107^{\circ}$. The sulfonic acid group could be eliminated from the former much more easily than from the latter. Dihydroretene could readily be regenerated from the sulfonic acid melting at $147-148^{\circ}$ by heating with water at 200° . On the other hand, the products obtained by treating the sulfonic acid melting at $106-107^{\circ}$ either with water or with concentrated hydrochloric acid, could not be definitely identified as dihydroretene.

Fusion of the alkali salts of the two monosulfonic acids with potassium hydroxide gave, in very low yields, two phenols. They were found to be identical with the retenols obtained from retene by Komppa and Wahlforss.⁴ This was established by preparing the acetyl and benzoyl derivatives of the phenols obtained from both hydrocarbons. This result indicated that dehydrogenation had occurred and implied that the sulfonic acid groups in the sulfonic acids of retene and dihydroretene were in analogous positions. In order to obtain further evidence the ethyl esters of A- and B-retenesulfonic acids were prepared and oxidized with chromic acid to the ethyl esters of retenequinonesulfonic acid. The ethyl esters of the two dihydroretenesulfonic acids were similarly oxidized. The quinonesulfonic ester thus obtained from the dihydroretenesulfonic acid melting at $147-148^{\circ}$ was identified, by melting point and the mixed melting point test as well as other characteristics, as the ethyl ester of A-retenequinonesulfonic acid. On the other hand, the properties of the quinonesulfonic acid ester obtained from the dihydroretenesulfonic acid melting at $106-107^{\circ}$ corresponded to those of the ester of B-retenequinonesulfonic acid. This shows, consequently, that in the sulfonation of dihydroretene the substituents enter positions analogous to those in A- and B-retenesulfonic acid. The new sulfonic acids were, therefore, designated as A-dihydroretenesulfonic acid and B-dihydroretenesulfonic acid. The addition of two hydrogen atoms has, therefore, apparently not changed the behavior of the retene nucleus toward substitution reactions.

method of degradation was discovered, we believe that, from certain properties of the compounds in the two series, the two retenols may be assigned structures which, if not definitely proved, are highly probable." (Abstractors' note.)

The acid chloride as well as the methyl and ethyl esters of both dihydroretenesulfonic acids were prepared. The acid chloride of A-dihydroretenesulfonic acid was reduced to the corresponding sulfinic acid and to the mercaptan.

During the course of this research it was found necessary to prepare a number of derivatives of retene. The description of the preparation of these compounds constitutes the last portion of the Experimental Part.

The following is a comparison of the derivatives of dihydroretene prepared in this investigation with the corresponding derivatives of retene.

TABLE I

Substituent	Dihydroretene derivatives, °C.		Retene derivatives, °C.	
	A-	B-	A-	B-
—SO ₂ OH + 2H ₂ O	147-148	106-107		
—SO ₂ OH			188-189 ⁴	121-123 ⁴
—SO ₂ Cl	91-92(82-83)	112-113	135-136	146.5-148 ⁴
—SO ₂ NH ₂	193-194	189-190		206-207.5 ⁴
—SO ₂ NHC ₆ H ₅	112-114	196-197		
—SO ₂ OCH ₃	98-99	85-86	164-166 ⁴	117-119 ⁴
—SO ₂ OC ₂ H ₅	72.5-73.5	78-79	137.5-138.5	114-115
Ditto quinone	183-184	169-171	183-184	170-170.5
—SO ₂ H	123-130			
—SH	185-188			
—SCOC ₆ H ₅	170-172			
—OH			200-202 ⁴	158-159 ⁴
—OCOCH ₃			160 ³	132-134 ⁴
—OCOC ₄ H ₉			177-178	112
—OCH ₃			147-148	115-116 ³

Frey⁶ obtained a mixture of diphenyl ketone and potassium phenanthrenesulfonate by boiling the potassium salt of phenanthrenequinone-sulfonic acid with aqueous potassium hydroxide. In order to determine whether the corresponding reaction occurred with retene derivatives, the potassium salts of A- and B-retenequinonesulfonic acids were boiled with aqueous potassium hydroxide. Potassium retenesulfonate, however, could not be identified among the products of the reaction. A mixture containing the potassium salt of a retene ketone monosulfonic acid was obtained from A-retenequinonesulfonic acid while retene ketone was the principal product from B-retenequinonesulfonic acid.

From the highest boiling fractions of pine tar (from *Pinus Sylvestris*) used as a raw material in this investigation, there was isolated a small amount of another, apparently new, hydrocarbon, possessing the formula C₂₄H₂₀.

Experimental Part

The retene used in these experiments was obtained from that fraction of pine tar boiling at about 360°. Besides retene, a small quantity (less than 1 g. from 500 g. of

⁶ Werner, *Ann.*, **321**, 345 (1902).

crude retene) of another hydrocarbon was isolated from this crude material in the course of recrystallization from petroleum ether. This substance crystallized from benzene in shining silver scales melting at 297–298° (uncorr.). This hydrocarbon was quite difficultly soluble in most solvents and appeared to be sulfonated by hot concentrated sulfuric acid. Analysis indicated the formula $C_{24}H_{20}$ for this hydrocarbon.

Anal. Calcd. for $C_{24}H_{20}$: C, 93.46; H, 6.54; mol. wt. 308.16. Found: C, 93.68, 93.83; H, 6.52, 6.35; mol. wt. (Rast),⁷ 306, 311.

Dihydroretene.—This compound was prepared essentially according to the method described by Virtanen.² The total yield of dihydroretene, m. p. 64–65°, amounted to 62.7% of the theoretical.

Dihydroretene Derivatives A-Series

A-Dihydroretenesulfonic Acid.—To 20 g. of dihydroretene heated on an oil-bath to 66–68° was added, with vigorous stirring, 20 g. of sulfuric acid (sp. gr. 1.84). The sulfonation was completed in fifteen minutes. The sulfonation mixture was then poured into 200 cc. of hot water and thoroughly agitated. Under these conditions the sirupy mass dissolved, forming a quite clear bright yellow solution. The ammonium salt of A-dihydroretenesulfonic acid precipitated immediately upon the addition of an excess of concentrated ammonium hydroxide. After standing overnight the salt was filtered off, washed with cold water and dried at 110°. The dried product was extracted with petroleum ether (b. p. 80–100°) in a Soxhlet extractor; yield 19.5 g. (69.1%).

The ammonium salt (10 g.) was dissolved in 150 cc. of a mixture of equal parts of pyridine and water. The solution was filtered and a warm aqueous solution of barium chloride was stirred in. The barium salt of the sulfonic acid which precipitated was filtered off, washed repeatedly with hot water and dried.

Of the barium salt obtained in this way, 11.5 g. was warmed and stirred with 80 cc. of glacial acetic acid until a homogeneous thin paste was obtained. Then 45 cc. of sulfuric acid (2 *N*) was gradually added and the mixture was heated nearly to boiling for ten minutes. Warm water (35 cc.) was then added and the solution filtered through a hot water funnel. The quite clear yellowish filtrate was concentrated *in vacuo* to about 75 cc. and 10 cc. of dilute sulfuric acid (1:1) added. On cooling the liquid solidified to a stiff white paste which could easily be filtered by suction. The shining scales of the sulfonic acid thus obtained were spread out on a porous plate. The acetic acid could be removed, almost completely, by allowing the product to stand over concentrated sodium hydroxide solution in a vacuum desiccator; yield, 7.6 g. The acid was obtained in the form of strongly refracting crystals melting at 147–148° by recrystallization from ether. The acid was titrated in aqueous alcohol solution with *N*/10 aqueous sodium hydroxide: calcd. for 0.1701 g. of $C_{18}H_{18}SO_3H + 2H_2O$: 4.83 cc.; found: 4.85 cc.

The acid lost its water of crystallization on standing over sulfuric acid in a vacuum desiccator.

Salts.—A number of salts of A-dihydroretenesulfonic acid were prepared and analyzed.

Methyl Ester.—Prepared by boiling the potassium salt with dimethyl sulfate for four minutes. Recrystallization from methyl alcohol gave slightly yellowish scales, m. p. 98–99°.

Anal. Calcd. for $C_{18}H_{22}SO_3$: C, 69.04; H, 6.71. Found: C, 68.81; H, 6.70.

Ethyl Ester.—Prepared by boiling the potassium salt with diethyl sulfate. Recrystallization from ethyl alcohol gave fine scales, m. p. 72.5–73.5°.

Anal. Calcd. for $C_{20}H_{24}SO_3$: C, 69.71; H, 7.03. Found: C, 69.18, 69.52; H, 7.06, 6.81.

⁷ Rast, *Ber.*, **55**, 1051 (1922).

TABLE II

Salt	H ₂ O of crystallization	Crystallized as	Dried at °C.	Solubility ^d	Analyses, anhydrous salt, %	
					Calcd.	Found
Na ^a	H ₂ O	Shiny scales	110	0.040	Na, 6.80	6.74
K ^b	H ₂ O	Thin prisms	110	.048	K, 11.04	10.87
NH ₄ ^a		Crystalline powder	110	.057	N, 4.20	4.10
					(Kjeldahl)	
Ba ^a		Crystalline powder	150	.0025	Ba, 17.89	17.79
Ca ^a		Crystalline powder	150	.005	Ca, 5.98	6.05
Cu ^b	2H ₂ O	Light green blue scales	150 ^c	.011	Cu, 9.16	8.84

^a Prepared from the free acid and the metallic hydroxide. ^b Prepared from the free acid and the metallic carbonate. ^c Lost its water of crystallization at 110°. ^d Grams of anhydrous salt per 100 g. of water at 17°.

To a solution of two grams of the ethyl ester in 50 cc. of glacial acetic acid gently heated on a water-bath was slowly added a warm solution of three grams of chromic acid in 30 cc. of glacial acetic acid. The solution was heated for forty-five minutes, allowed to cool and poured into cold water. The precipitate which formed was filtered off and dried on a porous plate; yield, 0.95 g. (44.0%).

Recrystallization from glacial acetic acid gave small light orange colored needles, m. p. 183–184°. These crystals exhibit complete identity in physical properties and appearance with the product obtained from the oxidation of ethyl A-retenesulfonate. A mixed melting point test of the two oxidation products showed no depression of the melting point. The substance was difficultly combustible.

Anal. Calcd. for C₂₀H₂₀SO₅: C, 64.48; H, 5.42. Found: C, 64.57, 63.24, 62.85; H, 6.00, 5.96, 6.66.

Chloride.—Prepared by treating potassium A-dihydroretenesulfonate with phosphorus pentachloride in the presence of a small amount of phosphorus oxychloride. The reaction was completed by warming for a short while on a water-bath. After cooling the reaction product was poured into ice water, extracted with ether and the ether solution was washed with water. Evaporation of the ether gave a yellow oil which quickly solidified; yield, 1.8 g. (95.3%). Recrystallization from benzene (b. p. 80–100°) gave thin star-shaped prisms, m. p. 91–92°.

In some cases a second modification of the chloride was obtained. This crystallized from benzene as dense granules which, despite repeated recrystallization, did not melt above 82–83°. Analysis gave values which agreed with those calculated for C₁₉H₁₉SO₂Cl. Both chlorides gave an amide, m. p. 193–194°, with ammonium hydroxide.

Anal. (Carius). Calcd. for C₁₉H₁₉SO₂Cl: Cl, 10.60; S, 9.58. Found: Cl, 10.41; S, 9.82.

Amide.—Prepared from the chloride of A-dihydroretenesulfonic acid and ammonium hydroxide; yield, 46.6%; colorless scales, m. p. 193–194°.

Anal. Calcd. for C₁₈H₂₁SO₂N: N, 4.44. Found: N, 4.49.

Anilide.—Prepared by boiling the chloride of A-dihydroretenesulfonic acid with aniline; yield, 51.3%. The anilide crystallized from alcohol in shining plates, m. p. 112–114°.

Anal. Calcd. for C₂₄H₂₅SO₂N: N, 3.58. Found: N, 3.40.

A-Dihydroretenesulfonic Acid.—The chloride of A-dihydroretenesulfonic acid (2 g.) was dissolved in 10 g. of toluene and 2 cc. of water added. The mixture was warmed and shaken on a water-bath while 3 g. of zinc dust was gradually added. A vigorous reaction began and the mass thickened to a stiff paste. Heating and stirring was continued, however, for a short while. After cooling, the mixture of the zinc salt

of the sulfinic acid and unchanged zinc dust was filtered off, washed with a little toluene, and dried. The residue was boiled with a solution of sodium carbonate in aqueous alcohol (1:1) and filtered. On cooling the sodium sulfinate crystallized in shining colorless scales; yield, 1.1 g. (57.1%). The salt is difficultly soluble in water.

Anal. Calcd. for $C_{13}H_{19}SO_2Na$: Na, 7.14. Found: Na, 7.13.

The sulfinic acid was freed from its sodium salt by concd. hydrochloric acid. Crystallization from aqueous alcohol gave white scales, m. p. 123–130°. The acid was titrated with *N*/10 sodium hydroxide: calcd. for 0.1110 g. of $C_{13}H_{19}SO_2H$: 3.70 cc.; found, 3.35 cc.

A-Dihydroretene Mercaptan.—The chloride of A-dihydroretenesulfonic acid was first reduced with zinc dust, giving the zinc sulfinate. This was further reduced in the cold with zinc dust in the presence of concd. hydrochloric acid. The mercaptan was obtained in the form of fine, light yellow scales, m. p. 185–188°; yield, 10.4%. As the substance seemed to be quite unstable, it was converted directly to the benzoyl derivative by means of benzoyl chloride in the presence of pyridine. In this way lemon yellow crystalline granules were obtained, m. p. 170–172°.

Anal. Calcd. for $C_{25}H_{24}SO$: C, 80.59; H, 6.50. Found: C, 80.74; H, 6.68.

Attempted Preparation of A-Dihydroretenol.—All attempts to replace the sulfonic acid group of potassium A-dihydroretenesulfonate, by means of alkali fusions, with the hydroxy group resulted in the formation of A-retenol. The yields were uniformly low; 15.6% from a fusion carried out in the usual manner. The retenol crystallized from xylene in the form of small glistening plates, m. p. 200–202°. With picric acid the picrate, m. p. 150–151°, was obtained in the form of ruby red needles.

Dihydroretene Derivatives, B-Series

B-Dihydroretenesulfonic Acid.—To 10 g. of dihydroretene heated on an oil-bath to 200° was added, with vigorous stirring, 10 g. of sulfuric acid (sp. gr. 1.84). The sulfonation was completed in five minutes. The sulfonation mixture was poured into 150 cc. of hot water and a slight excess of concentrated ammonium hydroxide was added to the hot solution. After standing overnight, 1.6 g. of a crystalline salt precipitated out. This was filtered off and the cloudy filtrate was extracted with ether. The clear aqueous solution was heated on a water-bath to remove the ether and then treated with a solution of 10 g. of potassium hydroxide in 30 cc. of water. When cooled, the potassium B-dihydroretenesulfonate crystallized in shining plates; yield, 5.78 g. (36.7%).

The first precipitate obtained with ammonium hydroxide was found to be mostly ammonium B-retenesulfonate.

Potassium B-dihydroretenesulfonate (5 g.) was dissolved in two liters of hot water and acidified with hydrochloric acid. An excess of barium chloride was added and the mixture was boiled for a few minutes. The precipitated barium B-dihydroretenesulfonate was filtered off, washed repeatedly with hot water and boiled for several hours with the calculated quantity of very dilute sulfuric acid. The barium sulfate was filtered off and the clear filtrate was concentrated, first on a water-bath and then *in vacuo* over sulfuric acid. This product, purified by recrystallization from benzene, gave slightly brownish colored scales, m. p. 105–106°, which, air dried, contained two molecules of water; both were lost when dried over sulfuric acid.

The free sulfonic acid was also obtained as nearly colorless scales, m. p. 106–107°, by saponifying the ethyl ester. The acid was titrated with *N*/10 potassium hydroxide: calcd. for 0.11 g. of $C_{13}H_{19}SO_3H + 2H_2O$: 3.12 cc.; found, 3.12 cc.

Salts.—A number of salts of B-dihydroretenesulfonic acid were prepared and analyzed.

TABLE III

Salt	H ₂ O of crystallization	Crystallized as	Dried at °C.	Solubility ^e	Analysis, anhydrous salt, % Calcd.	Found
K ^a	H ₂ O	Shiny scales	150 ^d	0.248	K, 11.04	10.75
NH ₄ ^b		Leaflets	110	7.73	N, 4.20	4.28
						(Kjeldahl)
Ba ^b	H ₂ O	Crystalline powder	130	0.026	Ba, 17.89	17.79
Ca ^b	6H ₂ O	Shiny scales	150	0.031	Ca, 5.98	5.82
Cu ^c	5.5H ₂ O	Green-blue needles	150	0.038	Cu, 9.16	8.86

^a Prepared from the free acid and potassium carbonate. ^b Prepared from the free acid and the metallic hydroxide. ^c Prepared from the ammonium salt and copper chloride. ^d Lost its water of crystallization at 110°. ^e Grams of anhydrous salt per 100 g. of water at 17°.

Methyl Ester.—Prepared by boiling the dried potassium salt with dimethyl sulfate. yield, 50.3%. Recrystallization from methyl alcohol gave small scales, m. p. 85–86°;

Anal. Calcd. for C₁₃H₂₂SO₃: C, 69.04; H, 6.71. Found: C, 68.72; H, 6.71.

Ethyl Ester.—Prepared by boiling the dried potassium salt with diethyl sulfate; yield, 82.3%. Recrystallization from ethyl alcohol gave long, colorless prisms, m. p. 78–79°.

Anal. Calcd. for C₂₀H₂₄SO₃: C, 69.71; H, 7.03. Found: C, 69.53; H, 7.10.

The ethyl ester was oxidized by chromic acid in a manner similar to that used for the oxidation of the corresponding A-derivative. Orange colored needles were obtained, m. p. 169–171°; yield, 58.5%. The crystals exhibited complete identity in physical properties and appearance with the ethyl B-retenequinonesulfonate obtained by oxidizing ethyl B-retenesulfonate. A mixed melting point test of the two oxidation products showed no depression of the melting point. The substance was difficultly combustible.

Anal. Calcd. for C₂₀H₂₀SO₃: C, 64.48; H, 5.42. Found: C, 64.10, 64.18; H, 5.40, 5.56.

Chloride.—Prepared by treating anhydrous potassium B-dihydroretenesulfonate with phosphorus pentachloride in the presence of phosphorus oxychloride, as in the case of the corresponding A-derivative; yield, 74.1%. Recrystallization from benzene gave yellowish, symmetrical crystals, m. p. 112–113°.

Anal. (Carius). Calcd. for C₁₈H₁₉SO₂Cl: Cl, 10.60; S, 9.58. Found: Cl, 10.72; S, 9.93.

Amide.—Obtained as small scales, m. p. 189–190°, from the chloride and ammonium hydroxide.

Anal. Calcd. for C₁₈H₂₁SO₂N: N, 4.44. Found: N, 4.10.

Anilide.—Prepared in a manner similar to that used for the preparation of the corresponding A-derivative. The anilide crystallized from alcohol in shining scales, m. p. 196–197°.

Anal. Calcd. for C₂₄H₂₆SO₂N: N, 3.58. Found: N, 3.58.

Attempted Preparation of B-Dihydroretenol.—All attempts to replace the sulfonic acid group of potassium B-dihydroretenesulfonate, by means of alkali fusions, with the hydroxy group resulted in the formation of B-retenol. The yields were uniformly low, 8.5% from a fusion carried out in the usual manner. After two crystallizations from alcohol–water, slightly yellowish scales of B-retenol, m. p. 158–159°, were obtained. The B-retenol was identified by means of its acetyl and benzoyl derivatives.

Retene Derivatives, A-Series

Ethyl A-Retenesulfonate.—Prepared from ammonium A-retenesulfonate and diethyl sulfate; yield, 61.7%; small, colorless leaflets, m. p. 137.5–138.5°.

Anal. Calcd. for $C_{20}H_{22}SO_2$: C, 70.12; H, 6.48. Found: C, 69.91; H, 6.52.

A-Retenesulfonyl Chloride.—Prepared from ammonium A-retenesulfonate, phosphorus pentachloride and phosphorus oxychloride; yield, 78.6%. Recrystallization from ether gave light yellow scales, m. p. 135–136°.

Anal. (Carius). Calcd. for $C_{19}H_{17}SO_2Cl$: Cl, 10.66; S, 9.64. Found: Cl, 10.52; S, 9.40.

Ethyl A-Retenequinonesulfonate.—Ethyl A-retenesulfonate was oxidized by chromic acid in a manner similar to that used for the oxidation of the corresponding dihydro derivative; yield, 39.4%. When crystallized from glacial acetic acid, small light orange yellow needles, m. p. 183–184°, were obtained. This substance, as was stated previously was identical with the product obtained by oxidizing ethyl A-dihydroretenesulfonate.

Action of Aqueous Potassium Hydroxide on Potassium A-Retenequinonesulfonate.—Potassium A-retenequinonesulfonate (6.8 g.) obtained from A-retenesulfonic acid, was boiled for three hours with about 120 cc. of a 50% solution of potassium hydroxide. The product was cooled and filtered. The residue was washed with water and dried on a porous plate. The light yellow product (5.5 g.) was separated by repeated recrystallization from aqueous alcohol into two fractions.

Fraction 1.—The more easily soluble portion, canary yellow in color, comprised about three-fifths of the original material. Analysis gave values which agreed with those calculated for potassium retene ketone sulfonate. Calcd. for $C_{17}H_{16}O_4SK$: C, 57.58; H, 4.27; K, 11.04. Found: C, 57.53; H, 4.56; K, 10.92. Esterification with diethyl sulfate resulted in the formation of small needles, m. p. 130°, insufficient in quantity for an analysis.

Fraction 2.—The more difficultly soluble portion consisted of an apparently crystalline light yellow powder. Analysis gave no conclusive evidence as to the composition of this product. After fusion with potassium hydroxide an acid which crystallized from benzene in the form of small scales melting at 160° was obtained. Analysis gave values which agreed with those calculated for methyl isopropyl diphenylmonocarboxylic acid. Calcd. for $C_{17}H_{16}O_2$: C, 80.27; H, 7.14. Found: C, 80.00; H, 7.16. The acid was titrated with *N*/10 potassium hydroxide: calcd. for 0.0637 g. $C_{16}H_{17}COOH$, 2.51 cc.; found, 2.30 cc.

A-Methoxyretene ($CH_3OC_{18}H_{17}$).—Prepared by heating an alcoholic solution of A-retenol and dimethyl sulfate in the presence of sodium hydroxide; yield, 63.1%. Crystallization from alcohol gave colorless needles melting at 147–148°.

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.31; H, 7.63. Found: C, 86.29; H, 7.78.

A-Benzoxyretene ($C_6H_5COOC_{18}H_{17}$).—Prepared from A-retenol and benzoyl chloride in pyridine solution; yield, 57.4%. When crystallized from alcohol the benzoyl derivative was obtained in the form of tufts of needles, moderately soluble in ether and melting at 177–178°.

Anal. Calcd. for $C_{25}H_{22}O_2$: C, 84.70; H, 6.26. Found: C, 84.84; H, 6.34.

Retene Derivatives, B-Series

Ethyl B-Retenesulfonate.—Prepared from ammonium B-retenesulfonate and diethyl sulfate; yield, 87.1%. Crystallization from alcohol gave small pointed scales, m. p. 114–115°.

Anal. Calcd. for $C_{20}H_{22}SO_2$: C, 70.12; H, 6.48. Found: C, 69.93; H, 6.54.

Ethyl B-Retenequinonesulfonate.—Ethyl B-retenesulfonate was oxidized in glacial acetic acid solution with chromic acid. Recrystallization of the oxidation product from glacial acetic acid gave small, orange colored needles, identical with those obtained by the oxidation of ethyl B-dihydroretenesulfonate, but distinctly darker than those obtained from the corresponding A-derivative.

Action of Aqueous Potassium Hydroxide on Potassium B-Retenequinonesulfonate.—A mixture of 7.6 g. of potassium B-retenequinonesulfonate and 40 cc. of 50% aqueous potassium hydroxide was refluxed for forty-five minutes. After cooling, the insoluble part was filtered off, washed with water and dried on a porous plate. Crystallization from alcohol gave sulfur-yellow flat prisms, m. p. 88–89°. Analysis gave values which agreed with those calculated for retene ketone, $C_{17}H_{16}O$; yield, 3 g. (62.2%). Calcd. for $C_{17}H_{16}O$: C, 86.39; H, 6.83. Found: C, 86.59; H, 6.60. For further identification the substance was reduced in alcohol solution by means of zinc dust in the presence of ammonium hydroxide. The retenefluorenyl alcohol thus obtained as pointed colorless scales, m. p. 132–133°, was analyzed. Calcd. for $C_{17}H_{18}O$: C, 85.66; H, 7.62. Found: C, 86.03; H, 7.41.

B-Benzoxylretene ($C_8H_7COOC_{13}H_{17}$).—Prepared from B-retenol and benzoyl chloride in pyridine solution; yield, 58.8%. Crystallization from alcohol gave well-developed plates, m. p. 112°.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 84.70; H, 6.26. Found: C, 84.72; H, 6.38.

Summary

The stability and aromatic character of dihydroretene as well as the similarity to retene in behavior has been studied.

Sulfonation gave two well-defined sulfonic acids which were isolated by means of their potassium salts. These were used in the preparation of a number of derivatives. In general they exhibited marked similarity in mode of preparation and in properties with the previously known A- and B-retenesulfonic acids. Oxidation of the ethyl esters of the A- and B-dihydroretenesulfonic acids resulted in the formation of the corresponding ethyl A- and B-retenequinonesulfonates. This showed that the sulfonic acid group had entered similar positions in the two hydrocarbons. Attempts to replace the sulfonic acid group of A- and B-dihydroretenesulfonic acid by the hydroxy group resulted in simultaneous dehydrogenation and consequent formation of the corresponding retenols.

For the purpose of comparison a number of additional derivatives of retene were prepared. The action of boiling aqueous potassium hydroxide on the potassium retenequinonesulfonates was studied. Retene ketone was obtained in good yield from potassium B-retenequinonesulfonate.

A new crystalline hydrocarbon, $C_{24}H_{20}$, m. p. 297–298° (uncorr.), occurring in small quantities with retene in the highest boiling fractions of pine tar, was isolated.

HELSINGFORS, FINLAND