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

SOME NEW MONOSUBSTITUTION DERIVATIVES OF RETENE

BY GUST. KOMPPA AND ERIC WAHLFORSS[1]

RECEIVED SEPTEMBER 18, 1930 PUBLISHED DECEMBER 18, 1930

Introduction and Historical

Retene is a hydrocarbon derived from pine tar. This compound, 8-methyl-2-isopropylphenanthrene, m. p. 98–99°, exhibits many peculiarities in its behavior toward ordinary chemical reagents. It is quite stable under certain conditions and will frequently react only if brought into solution and agitated vigorously.

Although a number of investigators have studied the effect of various reagents upon retene, the preparation of only one crystalline mono-substituted product has been reported. This, a monocarboxylic acid, $C_{18}H_{17}$-COOH, m. p. 121–123°, was obtained by Liebermann and Zsuffa[2] by the action of oxalyl chloride, in the presence of aluminum chloride, on a solution of retene in carbon disulfide. Repetition of this experiment from the meager description given resulted, in this research, in the formation of a well-characterized monocarboxylic acid, which after thorough purification and recrystallization melted over 100° higher, 229–231°.

Ekstrand[3] obtained a yellowish oil analyzing for a monochlororetene, $C_{18}H_{17}Cl$, by the action of chlorine gas on crystalline retene. No other monohalogen substitution products of retene have been reported.

The action of nitric acid on retene has been investigated extensively. Concentrated as well as fuming nitric acid readily attacks retene but no crystalline nitro derivatives have thus far been obtained.

The effect of sulfuric acid on retene has been studied by a number of investigators. Knauss[4] observed that sulfur dioxide was evolved when retene was heated with concentrated sulfuric acid above 100°. Apparently, however, no sulfonic acid was formed as no soluble barium salt could be isolated. Fritzsche[5] was able to isolate the barium salt of a disulfonic acid, $C_{18}H_{16}(SO_3H)_2$, obtained by the action of a mixture of concentrated and fuming sulfuric acid on retene. Ekstrand[3] was able to identify the free disulfonic acid and its chloride. All his attempts to prepare a monosulfonic acid, despite the use of the most diverse experimental conditions, were fruitless.

---

[1] Abstracted from a thesis presented by Eric Wahlforss in January, 1924, to the Faculty of Philosophy of the University of Helsingfors, Finland, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Acknowledgment is made to Dr. L. A. Goldblatt of the University of Pittsburgh in appreciation of the assistance rendered in abstracting this paper from the original Swedish thesis.

[2] Liebermann and Zsuffa, *Ber.*, **44**, 857 (1911).

[3] Ekstrand, *Ann.*, **185**, 81 (1877).

[4] Fehling, *ibid.*, **106**, 391 (1858).

[5] Fritzsche, *J. prakt. Chem.*, **82**, 335 (1861).

Results and Discussion

A well-characterized monocarboxylic acid, $C_{18}H_{17}COOH$, m. p. 229–231° was prepared by the method of Liebermann and Zsuffa.[2]

The methyl ester of this acid, $C_{18}H_{17}COOCH_3$, m. p. 96–97°, and the amide, $C_{18}H_{17}CONH_2$, m. p. 224–226°, were prepared. A monocarboxylic acid of retenequinone, $C_{18}H_{15}O_2COOH$, m. p. above 237°, was prepared by the action of chromic acid on the monocarboxylic acid dissolved in glacial acetic acid. This shows that the carboxyl group does not enter the 9- or 10-position in retene.

Attempts to chlorinate retene at 120–130 and 170–180° and to brominate retene dissolved in carbon tetrachloride both in the presence and absence of iodine resulted in the formation of a great variety of products with varying halogen contents but no definite compound could be isolated.

A viscous yellowish oil was obtained when retene dissolved in carbon tetrachloride was chlorinated with chlorine gas. Analysis indicated the formula $C_{18}H_{17}Cl$ for this product. It distilled at a constant temperature of 350–351° at atmospheric pressure but a high percentage of the original oil resinified. The wide range of boiling point, 195–205°, when this product was distilled at 10 mm. pressure would indicate the presence of a mixture. The insolubility of this oil in alcohol together with its analysis and its behavior when subjected to sulfonation indicated that it was at least not a mixture of retene and higher chlorinated derivatives. Oxidation of monochlororetene with chromic acid in acetic acid solution resulted in the formation of retenequinone. This indicates that the chlorine substitutes in the 9- or 10-position in retene.

Boiling the chlorinated product with alcoholic potassium hydroxide and with quinoline did not split off hydrogen chloride. The chlorine atom could not be replaced by iodine by treatment with sodium iodide in acetone or glacial acetic acid solution. No crystalline products were obtained when the monochlororetene was nitrated or sulfonated. Attempts to obtain monohydroxyretene from monochlororetene by Grignard's reaction resulted in the formation of traces of oil which were insoluble in water, aqueous sodium carbonate and mineral acids but soluble in aqueous sodium hydroxide. This oil gave the Liebermann test for phenols.

Methylretene, which could be considered as a link between retene and the resin acids, is of considerable theoretical significance. Attempts to prepare this compound from monochlororetene and methyl iodide with sodium in absolute ether were, however, unsuccessful.

Attempts to prepare a crystalline nitro derivative of retene by the action of nitric acid on retene dissolved in glacial acetic acid; acetyl nitrate in acetic anhydride solution and benzoyl nitrate in carbon tetrachloride solution were all unsuccessful. In one case traces of a yellow nitro derivative, 0.01 g., m. p. 154.5–156.5°, were obtained from 5 g. of retene by the action of acetyl nitrate in carbon tetrachloride solution.

Although retene was sulfonated with chlorosulfonic acid in boiling chloroform solution, no pure crystalline monosulfonic acid was obtained in this research. Two isomeric monosulfonic acids, $C_{18}H_{17}SO_3H$, designated as A-retenesulfonic acid and B-retenesulfonic acid, were obtained by adding concentrated sulfuric acid to vigorously stirred melted retene. Lower temperatures favored the formation of the A-retenesulfonic acid, m. p. 188–189°, and higher temperatures favored the formation of the B-retenesulfonic acid, m. p. 121–123°.

Attempts to isolate and separate the two monosulfonic acids by means of the alkaline earth and lead salts were unsuccessful as, contrary to the general rule for sulfonic acids, these salts are only very slightly soluble in hot water. The sodium, potassium and ammonium salts, however, differ enough in solubility from the other products formed during sulfonation to permit separation. The salts of the B-retenesulfonic acid are much more soluble than the corresponding salts of the A-retenesulfonic acid. The free B-retenesulfonic acid was obtained by the action of sulfuric acid on its barium salt. A-retenesulfonic acid again was isolated directly from the sulfonation mixture.

The formation of quinones, $C_{18}H_{15}O_2SO_3H$, when both the A-retenesulfonic acid and B-retenesulfonic acid were oxidized with chromic acid in acetic acid solution shows that the sulfonic acid group does not enter the 9- or 10-position in retene. Alkaline permanganate is decolorized by the potassium salts of the retenesulfonic acids but no crystalline oxidation products could be isolated.

A number of metallic salts of both retenesulfonic acids were prepared and analyzed. They crystallize with varying amounts of water of crystallization. Fusion of the ammonium sulfonates with alkali leads to the formation of monohydroxy derivatives. The term *retenol* is suggested for monohydroxyretene, $C_{18}H_{17}OH$, in analogy with the corresponding term for monohydroxyphenanthrene.

The methyl ester, $C_{18}H_{17}SO_3CH_3$, m. p. 164–166°, and A-retenol, $C_{18}H_{17}OH$, m. p. 200–202°, were obtained in good yields from the ammonium salt of A-retenesulfonic acid. The picrate of A-retenol melted at 151–152°.

A number of derivatives of B-retenesulfonic acid were prepared. The chloride, $C_{18}H_{17}SO_2Cl$, m. p. 146.5–148°; the amide, $C_{18}H_{17}SO_2NH_2$, m. p. 206–207.5°; the methyl ester, $C_{18}H_{17}SO_3CH_3$, m. p. 117–119° and the potassium salt of the quinone, $C_{18}H_{15}O_2SO_3K$, were obtained in crystalline form. B-retenol, $C_{18}H_{17}OH$, m. p. 158.5–159°, was prepared by fusing the ammonium salt of B-retenesulfonic acid with potassium hydroxide. Its picrate melted at 145–146°, and its acetyl compound, $C_{18}H_{17}OCOCH_3$, at

132–134°. B-retenol when coupled with diazobenzenesulfonic acid developed an orange-red color.

Two attempts to acetylate retene with acetyl chloride in carbon disulfide solution in the presence of aluminum chloride gave no positive results. These, together with other experiments of a negative nature, are omitted from the Experimental Part.

The following derivatives have been prepared in this investigation.

Derivatives	Melting point, °C.		
	A =	B =	
$C_{18}H_{17}SO_2OH$	188–189	121–123	
$C_{18}H_{17}SO_2Cl$		146.5–148	
$C_{18}H_{17}SO_2NH_2$		206–207.5	
$C_{18}H_{17}SO_2OCH_3$	164–166	117–119	
$C_{18}H_{17}OH$	200–202	158.5–159	
$C_{18}H_{17}OH$ picrate	151–152	145–146	
$C_{18}H_{17}OCOCH_3$		132–134	
$C_{18}H_{17}COOH$			229–231
$C_{18}H_{17}CONH_2$			224–226
$C_{18}H_{17}COOCH_3$			96–97

Experimental Part

The retene used in these experiments was obtained from that fraction of pine tar boiling above 300°. After purification it possessed a uniform melting point of 98–99°.

Monochlororetene.—A solution of 40 g. of retene in 200 g. of carbon tetrachloride to which a trace of iodine had been added was cooled to 0°. Chlorine gas was then passed through the solution until an increase in weight of 12.2 g. was noted. The solution was allowed to stand overnight at room temperature and was then washed successively with aqueous sodium bisulfite, sodium hydroxide and water. After drying with calcium chloride, the solvent was distilled off and the residue was rectified under reduced pressure. In this way 36.5 g. (79.5% yield) of a yellowish oil boiling at 195–205° (10 mm.) was obtained.

Anal. (Carius) Calcd. for $C_{18}H_{17}Cl$: Cl, 13.20. Found: Cl, 13.13.

This product is nearly insoluble in alcohol but is soluble in ether and petroleum ether. It distilled at 350–351° at atmospheric pressure (747.6 mm.) without appreciable decomposition but left a considerable residue of tar in the distilling flask. A small amount of chlorine-free substance crystallized out on standing. After one recrystallization from alcohol this melted at 94–97°. Mixed with retene, m. p. 98.5°, it melted at 96–97°. The distillate was boiled with alcohol to remove any traces of retene. The residue, d_4^{20} 1.1359, was analyzed for chlorine.

Anal. Calcd. for $C_{18}H_{17}Cl$: Cl, 13.20. Found: Cl, 13.30.

The results of refluxing this product for twenty-five hours with 33% alcoholic potassium hydroxide and for half an hour with quinoline indicated that it was not a mixture of retene and retene dichloride.

Oxidation of Monochlororetene.—A solution of 1.1 g. of monochlororetene in 3.5 g. of glacial acetic acid was treated with a solution of 1.9 g. of chromic acid in 10 g. of glacial acetic acid. The mixture was refluxed for half an hour. On cooling 0.4 g. (37.0% yield) of red chlorine-free needles separated out. The melting point, 190–192°, and appearance indicated that this was retenequinone.

Retenecarboxylic Acid and Derivatives

Retenecarboxylic Acid.—To a solution of 10 g. of retene in 75 cc. of freshly purified carbon disulfide, cooled to −4°, were added 23.4 g. of oxalyl chloride and 5 g. of finely pulverized aluminum chloride. After three hours an additional 75 cc. of carbon disulfide and 10 g. of aluminum chloride were added. The mixture was then left at room temperature. When after two weeks no more hydrogen chloride was evolved, the carbon disulfide was filtered off and the residue extracted with ether. The solvent was distilled and the residue boiled with aqueous sodium carbonate. The sodium salt of the carboxylic acid separated out from the solution; yield, 4.4 g. (31.6%). The free carboxylic acid was obtained by boiling the aqueous solution of the sodium salt with very dilute hydrochloric acid. After three crystallizations from benzene the acid melted at 229–231°. The acid is difficultly soluble in ether, more easily soluble in boiling benzene. It was titrated in alcohol solution with $N/10$ potassium hydroxide: calcd. for 0.1130 g. $C_{18}H_{17}COOH$: 4.06 cc.; found: 3.95 cc.

Sodium Salt.—This salt was prepared by neutralizing an alcohol solution of the free acid with $N/10$ aqueous sodium hydroxide.

The alcohol was distilled off and the salt recrystallized from water. The shining silver scales thus obtained were difficultly soluble in cold water but more easily soluble in hot water. They contain five molecules of water of crystallization, all of which are entirely lost below 136°. After drying the salt was analyzed.

Anal. Calcd. for $C_{18}H_{17}COONa$: Na, 7.66. Found: Na, 7.50.

Methyl Ester.—This compound was prepared by refluxing the sodium salt with dimethyl sulfate for five minutes. After recrystallization from alcohol a 51.7% yield of fine, slightly yellow scales, m. p. 96–97°, was obtained.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.15; H, 6.90. Found: C, 81.70; H, 6.75.

Amide.—This compound was prepared from the acid chloride. A mixture of 0.24 g. of retenecarboxylic acid, 1 g. of phosphorus oxychloride and 0.5 g. of phosphorus pentachloride was heated on a water-bath for ten minutes. The resulting mixture was cooled and poured into ice water. The undissolved part was filtered off, washed, dried in a desiccator and extracted with ether. The ether extract was washed with water, and the ether evaporated, leaving the solid acid chloride; yield, 0.14 g. (54.7%). It was dissolved in benzene and shaken with concentrated ammonium hydroxide. The precipitated amide was filtered off and recrystallized from benzene, m. p. 224–226°.

Retenequinonecarboxylic Acid.—To a solution of 0.2 g. of the dried sodium salt in 1 g. of glacial acetic acid was added in small portions a solution of 0.38 g. of chromic acid in 3.5 g. of glacial acetic acid. The mixture was refluxed for twenty minutes. On cooling the retenequinonecarboxylic acid separated out in long needles; yield, 0.13 g. (63.4%). This substance was boiled with hydrochloric acid and recrystallized from glacial acetic acid; m. p. 237–240°. Owing to the dark red color of the acid it was difficult to determine the melting point. When dried for two days over sulfuric acid no loss in weight was observed. The acid was slightly soluble in water and ether, somewhat more soluble in alcohol. It was titrated in very dilute alcohol solution with $N/100$ potassium hydroxide: calcd. for 0.0423 g. of $C_{18}H_{15}O_2COOH$: 13.7 cc.; found: 13.0 cc.

Monosulfonic Acids and Derivatives

A-Retenesulfonic Acid.—To 10 g. of retene heated on an oil-bath to 99° was added 10 g. of sulfuric acid (sp. gr. 1.84). The acid was at room temperature and was added slowly, with vigorous stirring, to the melted retene. The sulfonation was completed in five minutes, as was indicated by complete solution of a sample in hot water. The sulfonation mixture was poured into 200 g. of hot water, allowed to cool to about 70°

and filtered. After some time a gelatinous mass formed and this was filtered off. The residue was washed first with very dilute sulfuric acid and then with cold water. After drying in a desiccator it was extracted with ether and the residue recrystallized from glacial acetic acid. This gave well-developed scales melting at 188–189°. The acid was titrated in alcohol solution with $N/10$ sodium hydroxide: calcd. for 0.1530 g. of $C_{18}H_{17}SO_3H$: 4.87 cc.; found: 4.75 cc.

Ammonium Salt.—The sulfonation mixture, prepared as above, was poured into 300 g. of hot water, cooled and extracted with ether. The aqueous solution was reheated and concentrated ammonium hydroxide was added. The thick precipitate of ammonium A-retenesulfonate which thus formed was filtered off, washed with water and dried at 135°; yield, 3.85 g. (28.4%).

Methyl Ester.—This compound was prepared by refluxing potassium A-retenesulfonate with dimethyl sulfate. This salt had been obtained by neutralizing an alcohol solution of the free acid with potassium hydroxide. An 88.2% yield was obtained. The thin small scales of the methyl ester after recrystallization from methyl alcohol melted at 164–166°.

Anal. Calcd. for $C_{19}H_{20}SO_3$: C, 69.46; H, 6.14. Found: C, 69.33; H, 6.02.

Potassium A-Retenequinonesulfonate.—To a solution of 0.9 g. of A-retenesulfonic acid in 25 g. of glacial acetic acid was added in small portions a solution of 0.9 g. of chromic acid in glacial acetic acid. The solution was refluxed for half an hour and allowed to cool. As nothing crystallized out, it was evaporated to 10 cc. and again cooled. As precipitation still did not take place the solution was heated and a slight excess of potassium hydroxide was added. On cooling a red substance precipitated. This was washed with cold water and dried in a desiccator; yield, 0.5 g. (45.7%). This product, potassium A-retenequinonesulfonate, was easily soluble in hot water.

Anal. Calcd. for $C_{18}H_{15}O_5SK$: K, 10.23. Found: K, 9.99.

A-Retenol.—To 10 g. of potassium hydroxide and a few drops of water, heated in a nickel crucible to 220°, was added slowly 1 g. of ammonium A-retenesulfonate. The temperature was then increased to 270° and the fused potassium compound of A-retenol floated to the top. Not more than fifteen minutes should elapse from the time of the first addition of the salt. The entire mixture was then poured on to a copper plate, allowed to cool and dissolved in 1000 cc. of hot water.

The solution was filtered through a warm water filter and the phenol was precipitated with dilute sulfuric acid. After carefully decanting the supernatant liquid, the precipitated A-retenol could readily be filtered. It was washed thoroughly with water and with dilute aqueous sodium carbonate, dried in a desiccator and extracted with ether. The ether solution was thoroughly washed with water and aqueous sodium carbonate. The ether extract gave 0.4 g. of solid phenol (53.0% yield). Fine yellowish needles melting at 200–202° were obtained after three crystallizations from xylene. A-retenol is easily soluble in ether, boiling benzene and xylene, soluble in warm alkali and alcohol, but insoluble in aqueous sodium carbonate and sodium bisulfite. The picrate of A-retenol was obtained by mixing equivalent quantities of alcohol solutions of the components. The ruby red needles of this compound melted at 151–152°. A-retenol gave a positive Liebermann test for phenols. Ferric chloride imparted a slightly green color to an alcohol solution of the phenol.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.35; H, 7.25. Found: C, 86.13; H, 7.22.

B-Retenesulfonic Acid.—To 10 g. of retene heated on an oil-bath to 200° was added 10 g. of sulfuric acid (sp. gr. 1.84). The acid was at room temperature and was added slowly with vigorous stirring. The sulfonation was completed in two minutes. The product was poured into 300 g. of hot water. The solution was boiled and an excess of concentrated ammonium hydroxide was added. It was cooled, allowed to stand for twenty-four hours and filtered. The precipitated ammonium salt was washed with cold water and dried; yield, 5.0 g. (35.4%). The salt was redissolved in hot water and boiled with aqueous sodium hydroxide. An excess of barium chloride was added to the solution of the sodium salt, made slightly acid with hydrochloric acid, and the barium salt was filtered off and washed thoroughly. After treatment with the calculated amount of sulfuric acid, the free B-retenesulfonic acid was obtained in the form of colorless scales. These, when dried for two weeks in a desiccator, melted at 121–123°. The acid was titrated with $N/10$ potassium hydroxide: calcd. for 0.1154 g. of $C_{18}H_{17}SO_3H$: 3.67 cc.; found: 3.65 cc.

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

Ammonium Salt.—Prepared from the free acid, m. p. 121–123°, and ammonium hydroxide. Solubility: 0.1082 g. of salt in 100 g. water at 17°; more soluble at 100°. The salt, which crystallized without water of crystallization, was dried at 150° and analyzed. Calcd. for $C_{18}H_{21}SO_3N$: C, 65.21; H, 6.39; S, 9.68; N, 4.23; found: C, 65.09; H, 6.34; S (Carius), 9.60; N (Kjeldahl), 4.11.

Sodium Salt.—Prepared from the free acid and aqueous sodium hydroxide. Crystallized from water in white scales, which, air dried, contained three molecules of water. Two molecules were lost at 110° and the third at 150°. Solubility: 0.0726 g. of the anhydrous salt in 100 g. of water at 17°; more soluble at 100°. The salt was dried at 150° and analyzed. Calcd. for $C_{18}H_{17}SO_3Na$: Na, 6.84; found: Na, 6.96.

Potassium Salt.—Prepared from the free acid and aqueous potassium hydroxide. Crystallized from water as crystalline powder without water of crystallization. Solubility: 0.0824 g. of salt in 100 g. of water at 17°; only slightly more soluble at 100°. The salt was dried at 150° and analyzed. Calcd. for $C_{18}H_{17}SO_3K$: K, 11.10; found: K, 11.00.

Barium Salt.—Prepared from the sodium salt and barium chloride. Precipitated as a crystalline powder which, air dried, contained two molecules of water; both were lost when dried over sulfuric acid. Solubility: 0.0848 g. of anhydrous salt in 100 g. of water at 17°; sparingly soluble at 100°. The salt was analyzed. Calcd. for $(C_{18}H_{17}SO_3)_2Ba$: Ba, 17.99; found: Ba, 17.70.

Strontium Salt.—Prepared from the sodium salt and strontium chloride. Precipitated as a crystalline powder, which, air dried, contained four molecules of water; all four molecules were lost when dried over sulfuric acid. Solubility: 0.1016 g. of anhydrous salt in 100 g. of water at 17°; sparingly soluble at 100°. The salt was anzlyzed. Calcd. for $(C_{18}H_{17}SO_3)_2Sr$: Sr, 12.27; found: Sr, 12.28.

Calcium Salt.—Prepared from the sodium salt and calcium chloride. Precipitated as a crystalline powder, which, air dried, contained four molecules of water; all four molecules were lost when dried over sulfuric acid. Solubility: 0.1166 g. of anhydrous salt in 100 g. of water at 17°; sparingly soluble at 100°. The salt was analyzed. Calcd. for $(C_{18}H_{17}SO_3)_2Ca$: Ca, 6.01; found: Ca, 6.00.

Copper Salt.—Prepared from the free acid and copper carbonate. Crystallized as light green scales, which, air dried, contained five molecules of water: all five molecules were lost below 150°. Solubility: 0.1572 g. of anhydrous salt in 100 g. of water at 17°; more soluble at 100°. The salt was analyzed. Calcd. for $(C_{18}H_{17}SO_3)_2Cu$: Cu, 9.21; found (CuO): Cu, 8.91.

Chloride.—Prepared from potassium B-retenesulfonate in a manner similar to that described for the chloride used in the preparation of retenecarboxylic acid amide; yield, 68.8%. Recrystallization from benzene gave colorless prisms, m. p. 146.5–148°.

Anal. (Carius) Calcd. for $C_{18}H_{17}SO_2Cl$: Cl, 10.66; S, 9.64. Found: Cl, 10.55; S, 9.79.

Amide.—Prepared from the chloride of B-retenesulfonic acid and ammonium hydroxide; yield, 31.9%; colorless scales, m. p. 206–207.5°.

Anal. Calcd. for $C_{18}H_{19}SO_2N$: N, 4.47. Found: N, 4.16.

Methyl Ester.—Prepared from ammonium B-retenesulfonate and dimethyl sulfate; yield, 73.8%. Recrystallization from methyl alcohol gave colorless needles, m. p. 117–119°.

Anal. Calcd. for $C_{19}H_{20}SO_3$: C, 69.46; H, 6.14. Found: C, 69.39; H, 6.02.

Potassium B-Retenequinonesulfonate.—To a solution of 2 g. of potassium B-retenesulfonate in 10 g. of glacial acetic acid was added, in small portions, a cold solution of 3.8 g. of chromic acid in 35 g. of glacial acetic acid. The solution was refluxed for about half an hour and on cooling 1.2 g. (55.3% yield) of orange colored scales crystallized out. This product, potassium B-retenequinonesulfonate, was easily soluble in hot water.

Anal. Calcd. for $C_{18}H_{15}O_5SK$: K, 10.23. Found: K, 10.01.

B-Retenol.—Prepared from ammonium B-retenesulfonate by the method used for A-retenol. The temperature, however, was not allowed to exceed 240°; yield, 66.37%. Recrystallization from xylene gave slighly yellowish scales, m. p. 158.5–159°. B-retenol is easily soluble in ether, alcohol, benzene and nitrobenzene; soluble in aqueous sodium hydroxide, but insoluble in sodium carbonate and sodium bisulfite. The picrate of B-retenol, small orange-red scales, melted at 145–146°. B-retenol gave a positive Liebermann test for phenols. Ferric chloride imparted a green color to an alcohol solution of the phenol.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.35; H, 7.25. Found: C, 86.14; H, 7.26.

Acetyl-B-retenol.—Prepared from B-retenol, alkali and acetic anhydride. Recrystallization from alcohol gave fern-like crystals, m. p. 132–134°.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.15; H, 6.90. Found: C, 82.09; H, 7.00.

B-Retenol Sodium Azobenzenesulfonate.—B-retenol readily coupled with diazobenzenesulfonic acid, giving a red dye which dyed, wool and silk cherry-red.

Summary

Only two mono-substituted derivatives prepared from retene have been reported previously in the literature: monochlororetene and a monocarboxylic acid, m. p. 121–123°. The preparation of mono-substituted products of retene has been the object of this investigation.

Sulfonation gave two well-defined monosulfonic acids. They were isolated by means of the ammonium or sodium salt. These were used in the preparation of a number of derivatives; the most interesting was the monohydroxy derivative, *retenol*. Only one retenol coupled with diazo compounds. An attempt to determine the position of the sulfonic acid group by oxidation with chromic acid resulted in the formation of retenequinonesulfonic acid, showing that this group did not enter the 9- or 10-position in retene. Chlorination of retene resulted in an oil, monochlororetene, the individuality of which was not definitely established. Oxidation of this product with chromic acid gave retenequinone. Action of oxalyl chloride on retene resulted in the formation of a monocarboxylic acid, m. p. 229–

231°. A few derivatives were prepared. Oxidation with chromic acid gave retenequinonecarboxylic acid.

HAMMERMILL PAPER COMPANY
ERIE, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE FORMATION OF A COMPLEX MIXTURE OF MANY RMgX COMPOUNDS FROM THE REACTION BETWEEN A SIMPLE RX COMPOUND AND MAGNESIUM

BY HENRY GILMAN AND NINA B. ST. JOHN

RECEIVED SEPTEMBER 18, 1930 PUBLISHED DECEMBER 18, 1930

Introduction

The simplest expressions for the reaction between an RX compound and magnesium in ether are the following

$$RX + Mg \longrightarrow RMgX \qquad (I)$$
$$2RX + Mg \longrightarrow R\cdot R + MgX_2 \qquad (II)$$

Reaction II is the chief side reaction in the preparation of Grignard reagents, and the extent of this reaction varies markedly with the nature of the RX compound, the relative proportions of reactants and experimental conditions.[1] The hydrocarbon (or their equivalent) by-products are not pure R·R compounds, but may contain R(+H) and R(–H) compounds[2] as well as R·R compounds having R-groups unlike those contained in the original RX compound.[3]

Furthermore, Reaction I gives an incomplete picture of the more important compounds contained in Grignard solutions inasmuch as these reagents are involved in the following equilibria[4]

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (III)$$
$$RMgX \rightleftharpoons R- + -MgX \qquad (IV)$$

In short, a Grignard reagent is not simply an RMgX compound, but a mixture of RMgX, R_2Mg, MgX_2, R– and –MgX[5] in a series of equilibria

---

[1] Gilman, Zoellner and Dickey, THIS JOURNAL, **51**, 1576, 1583 (1929); Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928); Gilman and Zoellner, THIS JOURNAL, **52**, 3984 (1930).

[2] Gilman and Fothergill, *ibid.*, **50**, 3334 (1928).

[3] Gilman and Kirby, *ibid.*, **51**, 1571 (1929).

[4] Gilman and Fothergill, *ibid.*, **51**, 3149 (1929); Gilman and Zoellner, *ibid.*, **52**, 3984 (1930). These articles contain leading references to other work. For recent related studies see Gomberg and Bachmann, *ibid.*, **52**, 2455 (1930); Bachmann, *ibid.*, **52**, 3287 (1930).

[5] Gilman and Brown, *ibid.*, **52**, 1128 (1930). This article contains leading references to the chemistry of the interesting magnesious halides or the binary systems (MgX_2 + Mg) of Gomberg and co-workers. Better reviews of these systems are to be had in the chapters entitled "Metallo-Organic Compounds," in Vol. III (1927–1928) and Vol. IV (1928–1929) of the Annual Survey of American Chemistry, published for the National Research Council by the Chemical Catalog Co. of New York.