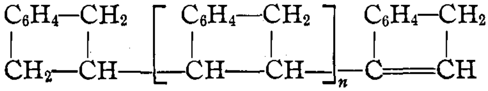
Summary

Indene is converted into high polymers by the catalytic action of antimony pentachloride and stannic chloride. The products are heterogeneous. The highest polymer isolated was represented by a fraction with a molecular weight corresponding to $(C_9H_8)_{29}$. The polymeric products obtained by heating indene are lower, the higher the temperature used. These products, too, are heterogeneous. There is a clear relationship between the melting point and molecular weight of polymers of indene.

All of the polyindenes, no matter what their molecular weight, contain one double bond per molecule. It is concluded that the polymerization of indene proceeds step-wise by the addition, involving the wandering of hydrogen, of successive molecules of the monomer, leading to products of the formula



$$\begin{array}{l} C_6H_4\text{—}CH_2 \\ |\qquad\quad | \\ CH_2\text{—}CH\text{—} \end{array}\left[\begin{array}{l} C_6H_4\text{—}CH_2 \\ |\qquad\quad | \\ \text{—}CH\text{—}CH\text{—} \end{array}\right]_n\begin{array}{l} C_6H_4\text{—}CH_2 \\ |\qquad\quad | \\ \text{—}C{=}CH \end{array}$$

Cinnamal fluorene yields high polymers when treated with antimony pentachloride or stannic chloride, the products being mixtures. Heating at 240–250° also causes it to polymerize. Cinnamal indene and benzal indene also can be polymerized by heat and by catalysts. Hydroxybenzyl benzal indene can be polymerized by antimony pentachloride.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE PREPARATION OF THE SULFONYLIDES OF CRESOL- AND CHLOROPHENOL DISULFONIC ACIDS

BY C. S. SCHOEPFLE, F. J. VAN NATTA AND R. G. CLARKSON

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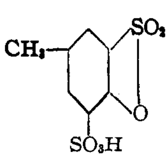
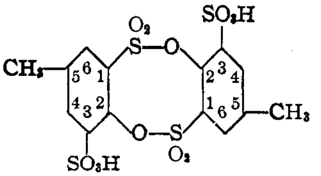
Raschig[1] found that *p*-cresol disulfonic acid was dehydrated by treatment with fuming sulfuric acid to give a product which was supposedly the monomolecular (*p*-cresol sulfone)-sulfonic acid (I).



(I)



(II)

In a very brief description of this compound, the fact was mentioned that it gave insoluble sodium and potassium salts which might be of value in analytical chemistry. Later,[2] Raschig concluded that his product was a disulfonic acid of *p*-methylphenylene-*o*-sulfonylide or, as it will

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[1] Raschig, *Z. angew. Chem.*, **25**, 1944 (1912); *Chem. Zeit.*, **36**, 1070 (1912).

[2] See Anschütz, *Ann.*, **415**, 65 (1918).

be named in this paper, (2-hydroxy-5-methyl-*m*-benzene disulfonic acid) sulfonylide (II). Examples of this class had been prepared previously by Schiff[3] and by Anschütz.[4] In order to establish the structure of this compound, Anschütz[2] prepared the corresponding sulfonyl chloride and found that its molecular weight in nitrobenzene agreed with the bimolecular sulfonylide formula.

The purpose of the present investigation was (1) to determine if the formation of sulfonylides is a general reaction for substituted phenols upon treatment with fuming sulfuric acid, (2) to obtain further proof of the bimolecular structure of these compounds and (3) to determine the solubility of the sodium salts.

It has been found that the sulfonylide described by Raschig can be prepared in 87% yield by heating *p*-cresol for several hours at 100° with fifteen times its weight of fuming sulfuric acid containing 20% of sulfur trioxide. Under similar conditions, sulfonylides were obtained from *o*-cresol, *o*-chlorophenol and *p*-chlorophenol in 80–85% yields, and from *m*-chlorophenol in 50% yield; no sulfonylide was obtained from *m*-cresol.

The corresponding sulfonyl chlorides, sulfonamides and the methyl esters of the sulfonylides of *p*-cresol disulfonic acid and of *o*-cresol disulfonic acid were prepared and attempts to determine their molecular weights were made. The molecular weights of the sulfonyl chlorides could not be obtained for, although they were soluble in boiling nitrobenzene, the solutions gradually darkened in color and in a short time became black, indicating decomposition. The sulfonamides were not sufficiently soluble to permit molecular weight determinations, but the esters proved to be more suitable. The methyl esters of the sulfonylides of *p*-cresol disulfonic acid and of *o*-cresol disulfonic acid both gave molecular weights in methyl alcohol which indicated a monomolecular structure. However, the molecular weight of the sulfonylide of *o*-cresol disulfonic acid in acetone and in acetic acid agreed with the bimolecular formula and the same was true of the corresponding methyl ester in acetone and in ethyl acetate. It appeared, therefore, as if the molecular weights of the esters in methyl alcohol were abnormal and in order to confirm this the dimethyl ester of *p*-cresol disulfonic acid was prepared and its molecular weight determined in methyl alcohol, acetone and ethyl acetate. The results showed that acetone and ethyl acetate gave the correct value but that the molecular weight in methyl alcohol was again abnormally low. The molecular weights were determined by the Menzies method[5] except in the case of acetic acid where the Beckmann ebullioscopic method was used.

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[3] Schiff, *Ann.*, **178**, 187 (1875).

[4] Anschütz, *Ber.*, **45**, 2378 (1912).

[5] Menzies and Wright, This Journal, **43**, 2314 (1921).

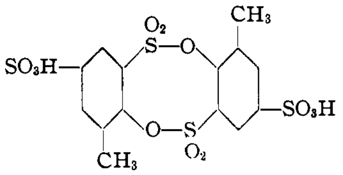
Rough solubility determinations were made for the sodium salts of the sulfonylides. The solubility of the sodium salt of the sulfonylide of *p*-chlorophenol disulfonic acid was found to be 1.6 g. per 100 g. of water at 25°, while the others varied in solubility from 0.6 g. to 0.9 g. per 100 g. of water. A mono-sulfonic acid of (6-hydroxy-*m*-toluene sulfonic acid) sulfonylide was prepared and its sodium salt proved to be soluble only to the extent of 0.13 g. per 100 g. of water at 25°. The alkali salts of the acids described in this paper are being investigated in this Laboratory by Dr. H. H. Willard in regard to their possible value in analytical chemistry.

Experimental Part

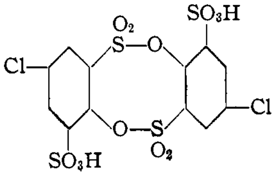
(2-Hydroxy-5-methyl-*m*-benzene Disulfonic Acid) Sulfonylide (II) has been described by Raschig,[1] who gave no details of the method of preparation, and also by Anschütz,[2] who heated *p*-cresol disulfonic acid at 100° with twice its weight of fuming sulfuric acid containing 60% of sulfur trioxide. In neither case was the yield stated. This sulfonylide and also the other sulfonylides described in this paper were obtained in good yields by treating the cresol or the chlorophenol with ten to fifteen times its weight of fuming sulfuric acid containing 20% of sulfur trioxide. Since the reaction is rather vigorous in its initial stage, the following general procedure was adopted.

Fifteen g. of 95% sulfuric acid was added to 10 g. of the cresol or chlorophenol and the solution heated on the steam-bath for a few minutes, after which it was cooled and treated with 135 g. of fuming sulfuric acid containing 25% of sulfur trioxide. The flask was then immersed in a steam-bath and heated for two to eight hours, during which time the sulfonylide usually crystallized. The crystals were very fine and difficult to filter; therefore the mixture was poured over ice, diluted with water and heated to about 100° when a clear solution was obtained—volumes ranging from 350 cc. to 700 cc. were required. When the solution cooled, the sulfonylide crystallized in colorless needles or in plates which were filtered, washed with 20% hydrochloric acid and dried in air. The water of crystallization was determined by drying the sample for twelve to twenty hours at temperatures varying from 120 to 145° depending upon the stability of the compound; however, in the case of (5-chloro-2-hydroxy-*m*-benzene disulfonic acid) sulfonylide, which could not be dried above 135° because of slight decomposition, a period of eighty hours was required before constant weight was obtained. All of the sulfonylides decompose above 300° without melting. They are soluble in water and in alcohol, soluble in some cases in acetone and in acetic acid, and insoluble in the other common organic solvents and in inorganic acids. They are all readily recrystallized from dilute hydrochloric acid.

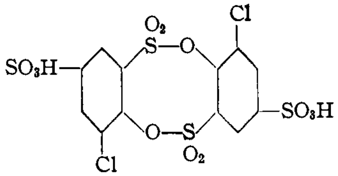
The following structures have been assigned to the sulfonylides on the basis that a hydroxyl group has a greater directing influence than a methyl group or a chlorine atom. The yields, the number of molecules of water of crystallization, the analyses and the crystalline forms of the sulfonylides are given in Table I.



(III)



(IV)



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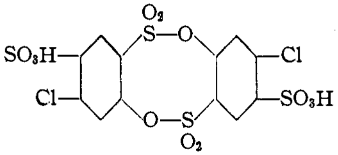

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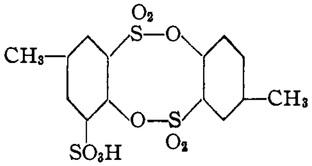

(VII)

TABLE I

DATA ON AND ANALYSES OF SULFONYLIDE DERIVATIVES OF *m*-BENZENE DISULFONIC ACID

Derivative	Time of heating, hours	Yield, %	Water of crystn., moles	Cryst. form	Sulfur, % Calcd.	Sulfur, % Found	Replaceable H,[a] % Calcd.	Replaceable H,[a] % Found	Water of crystn., % Calcd.	Water of crystn., % Found
2-Hydroxy-5-methyl (II)	2	87	4[b]	Needles	22.41	22.15	0.352	0.345	12.59	12.62
4-Hydroxy-5-methyl (III)[c,d]	6	80	6	Elon. plates	21.08	20.72	.331	.333	17.76	17.71
5-Chloro-2-hydroxy (IV)	6	84	4	Elon. plates	20.91	20.84	.329	.329	11.75	11.76
5-Chloro-4-hydroxy (V)	6	83	6	Plates	19.75	19.50	...		16.65	16.58
6-Chloro-4-hydroxy (VI)[f]	8	49	8	Plates	18.71	18.55	.294	.302	21.03	20.81

[a] By titration with standard sodium hydroxide solution.

[b] Anschütz found three molecules of water of crystallization.

[c] Molecular weight in acetone ($K = 17.2$): 505, 528; in acetic acid ($K = 30.7$): 495, 485. Calcd. for $C_{14}H_{12}O_{12}S_4$: 500.4.

[d] This sulfonylide has been prepared by Pollak and Gebauer-Fülnegg (ref. 8) by treating *o*-cresol with chlorosulfonic acid and is described by them as an amorphous powder which could not be obtained in crystalline state. Since the sulfonylide crystallizes beautifully from dilute inorganic acids, their product could not have been pure.

[e] Results were high due to partial hydrolysis of the sulfonylide upon titration.

[f] This compound was prepared by heating *m*-chlorophenol with 15 times its weight of fuming sulfuric acid containing 25% of sulfur trioxide.

Disulfonamide of (2-Hydroxy-5-methyl-*m*-benzene Disulfonic Acid) Sulfonylide.— The corresponding disulfonyl chloride[2] was obtained in quantitative yield by heating the sulfonylide with phosphorus pentachloride for one hour at 130°, adding enough phosphorus oxychloride to keep the mixture fluid. The compound was purified by recrystallization from benzene with a Soxhlet extractor. It was soluble in hot nitrobenzene but decomposed slowly in boiling nitrobenzene so that its molecular weight could not be obtained.

Ten g. of the crude, dry disulfonyl chloride was suspended in 150 cc. of nitrobenzene, the flask immersed in an oil-bath at 175–180° and a vigorous stream of dry ammonia passed into the mixture for one hour. The precipitate was filtered, washed with alcohol and then washed thoroughly with water to remove the ammonium chloride; yield, 8.5 g. (92%). The disulfonamide is insoluble in water and the common organic solvents, but can be recrystallized from acetone or acetic acid by means of a Soxhlet extractor. Very fine, colorless needles were obtained which decompose above 300° without melting.

Anal. Calcd. for $C_{14}H_{14}O_{10}S_4N_2$: S, 25.73; N, 5.62. Found: S, 25.44; N (Kjeldahl), 5.58.

Diethyl Ester of (2-Hydroxy-5-methyl-*m*-benzene Disulfonic Acid) Sulfonylide.—Ten g. of the anhydrous silver salt of the sulfonylide was suspended in 125 cc. of absolute ethyl alcohol, 10 g. of ethyl iodide added and the mixture refluxed on the steam-bath for several hours. The precipitated silver iodide was filtered and the solution poured slowly into absolute ether, whereby the ester was obtained in fine, colorless, elongated plates; yield, 7.6 g. (97%). It is soluble in ethyl alcohol and in hot methyl alcohol, but insoluble in ether, benzene, acetone, ethyl acetate, chloroform and acetic acid. The ester is rapidly hydrolyzed in water even at room temperature; consequently titration with standard alkali affords the most convenient method of analysis.

Anal. 0.7216 g. required 25.16 cc. of $N/10$ NaOH. Calcd. for $C_{18}H_{20}O_{12}S_4$: 25.94 cc. S, calcd.: 23.05. Found: 22.32.

Both analyses gave values about 3% low, due probably to a small amount of alcohol either occluded in the crystals or held as alcohol of crystallization. Drying in vacuum did not remove this alcohol, and heating to 90° caused decomposition into the corresponding sulfonylide and ethylene.[6] The ester when recrystallized from methyl alcohol contained two molecules of methyl alcohol of crystallization.

Dimethyl Ester.—The dimethyl ester was prepared in 95% yield by treating the anhydrous silver salt with methyl iodide, following the procedure described for the preparation of the ethyl ester. The absolute methyl alcohol which was used as the solvent was prepared by dissolving magnesium in the alcohol and distilling from the magnesium methylate which was formed.[7] The ester was obtained in fine, colorless crystals by pouring the methyl alcohol solution into ether, or by concentrating the solution. The crystals contain two molecules of methyl alcohol of crystallization which is given off readily at a temperature of 90°. It chars without melting when heated above 250°. The ester is soluble in methyl and ethyl alcohol, and insoluble in the other common organic solvents.

Anal. 0.3770 g. required 14.25 cc. of $N/10$ NaOH. Calcd. for $C_{16}H_{16}O_{12}S_4$: 14.27 cc. S, calcd.: 24.27. Found: 23.97. Molecular weight in methyl alcohol ($K = 8.8$): 271, 295. Calcd.: 528.4.

Disulfonamide of (4-Hydroxy-5-methyl-*m*-benzene Disulfonic Acid) Sulfonylide.—The disulfonyl chloride of this sulfonylide has been described by Pollak and Gebauer-Fülnegg,[8] who prepared it by treating *o*-cresol with chlorosulfonic acid. We obtained the compound in quantitative yield by heating the sulfonylide with phosphorus pentachloride, using phosphorus oxychloride as the solvent. Ten g. of the crude, dry disulfonyl chloride was suspended in 150 cc. of nitrobenzene and dry ammonia passed into the mixture for one hour at a temperature of 100°. The precipitate was filtered, washed with alcohol and then washed thoroughly with water. The disulfonamide was recrystallized from acetic acid using a Soxhlet extractor and was obtained in small, colorless crystals which decompose above 300° without melting; yield, 8.8 g. (95%). The compound is slightly soluble in hot acetic acid and in acetone, and is insoluble in the other common organic solvents.

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[6] Foldi, *Ber.*, **60B**, 656 (1927).

[7] Bjerrum and Zechmeister, *Ber.*, **56**, 894 (1923).

[8] Pollak and Gebauer-Fülnegg, *Monatsh.*, **46**, 387 (1925).

Anal. Calcd. for $C_{14}H_{14}O_{10}S_4N_2$: S, 25.73; N, 5.62. Found: S, 25.51: N (Kjeldahl), 5.59.

Dimethyl Ester of (4-Hydroxy-5-methyl-*m*-benzene Disulfonic Acid) Sulfonylide.—Ten g. of the anhydrous silver salt of the sulfonylide and 7.5 g. of methyl iodide in absolute methyl alcohol were heated for one hour on the steam-bath. The precipitated silver iodide was filtered, the solution concentrated under reduced pressure and the residue dissolved in hot ethyl acetate. Upon cooling, the ester was obtained in colorless crystals containing two molecules of methyl alcohol of crystallization; yield, 7.6 g. (92%). The alcohol of crystallization is given off slowly at a temperature of 60°; drying at temperatures above 90° usually results in decomposition. The compound chars above 250° without melting. It is soluble in methyl and ethyl alcohol and in acetone, slightly soluble in ethyl acetate and insoluble in ether, benzene and carbon tetrachloride.

Anal. 0.4562 g. required 17.26 cc. of $N/10$ NaOH. Calcd. for $C_{16}H_{16}O_{12}S_4$: 17.27 cc. S, calcd.: 24.27. Found: 23.87. Molecular weight in methyl alcohol: 261, 278; in acetone: 507, 517; in ethyl acetate ($K = 27.9$): 495, 530. Calcd.: 528.4.

(6-Hydroxy-*m*-toluene Sulfonic Acid) Sulfonylide-5-sulfonic Acid (VII).—(6-Hydroxy-*m*-toluene sulfonic acid) sulfonylide was prepared by the action of phosphorus oxychloride on *p*-cresol sulfonic acid as described by Anschütz.[2] It was found that the crude sulfonic acid obtained from the sulfonation of *p*-cresol could be used without further purification. Fifty g. of *p*-cresol was treated with an equal weight of 100% sulfuric acid and the mixture heated for one hour on the steam-bath. The sulfonic acid which crystallized when the solution cooled was sucked as dry as possible on a porous glass filter and then heated for six hours on the steam-bath with twice its weight of phosphorus oxychloride. The mixture was cooled and decomposed with ice, whereupon the sulfonylide was obtained as a sticky mass which hardened to a solid. The lumps were boiled in acetic acid, from which the sulfonylide was recovered in small, colorless crystals; yield, 20 g. (25%).

Five g. of the sulfonylide was treated with 50 g. of fuming sulfuric acid containing 25% of sulfur trioxide and the mixture allowed to stand at room temperature until a clear solution was obtained. It was then poured over ice and the sulfonic acid which was precipitated was sucked as dry as possible on a funnel and recrystallized from acetic acid. Colorless, elongated plates were obtained which melted at 220–222°, depending upon the rate of heating. The air-dried crystals contain approximately two molecules of water of crystallization; yield, 4.3 g. (64%). The compound is soluble in alcohol and in hot acetic acid, slightly soluble in hot water and in hot acetone, and insoluble in ether, benzene, ethyl acetate, carbon disulfide and carbon tetrachloride. This acid presents a rather unusual phenomenon in that a solution in hot water sets to a gel on cooling. Titration with standard alkali gave high results, due to hydrolysis of the sulfonylide; the results with sodium carbonate solution were somewhat better but were not entirely satisfactory.

Anal. Calcd. for $C_{14}H_{12}O_9S_3 . 2H_2O$: S, 21.08; H_2O, 7.90. Found: S, 20.74; H_2O, 7.75 (loss in weight on drying for four hours at 145°). Molecular weight in acetic acid: 363. Calcd. for $C_{14}H_{12}O_9S_3$: 420.3.

Methyl Ester of (6-Hydroxy-*m*-toluene Sulfonic Acid) Sulfonylide-5-sulfonic Acid.—Ten g. of the anhydrous silver salt and 5 g. of methyl iodide in 300 cc. of absolute methyl alcohol were heated on the steam-bath for several hours. The precipitated silver iodide was filtered and the solution allowed to cool, whereupon colorless crystals of the ester were obtained. The crystals contained about one and one-half molecules of methyl alcohol of crystallization, which was given off upon drying at 90°; yield, 7.2 g. (87%). When heated to higher temperatures, the ester decomposed without charring to give the sulfonic acid, which then melted at about 220°. The compound is soluble in ethyl alcohol, fairly soluble in hot methyl alcohol, slightly soluble in hot acetone and insoluble in ether, benzene, ethyl acetate, carbon disulfide and carbon tetrachloride.

Anal. Calcd. for $C_{15}H_{14}O_9S_3$: S, 22.15. Found: 22.09. Molecular weight in ethyl alcohol ($K = 11.7$): 412. Calcd.: 434.3.

Dimethyl Ester of 2-Hydroxy-5-methyl-*m*-benzene Disulfonic Acid.—Ten g. of the anhydrous silver salt of 2-hydroxy-5-methyl-*m*-benzene disulfonic acid[9] and 8 g. of methyl iodide were added to about 75 cc. of absolute methyl alcohol in a stoppered flask and allowed to stand for several hours with occasional shaking. The precipitated silver iodide was filtered, the alcohol distilled off as completely as possible under reduced pressure at 50–60°, and the residue dissolved in a small amount of hot methyl benzoate. Upon cooling, the ester was obtained in small, colorless crystals which were filtered and washed with methyl benzoate and benzene. A further crop of crystals was obtained by adding benzene to the filtrate. The crystals contained methyl alcohol of crystallization which was given off upon drying at 80°; yield, 5.3 g. (86%); m. p. 148–149°. The ester is soluble in alcohol and acetone, slightly soluble in ether and in ethyl acetate and insoluble in benzene, petroleum ether, carbon disulfide and carbon tetrachloride.

Anal. 0.2009 g. required 13.28 cc. of $N/10$ NaOH. Calcd. for $C_9H_{12}O_7S_2$: 13.56 cc. S, calcd.: 21.65. Found: 21.41. Molecular weight in methyl alcohol: 190, 192; in acetone: 297, 305; in ethyl acetate: 295, 305. Calcd.: 296.2.

Solubility of the Sodium Salts.—A solution of the recrystallized sodium salt was prepared of sufficient concentration so that, upon cooling, part of the salt would crystallize. The flask was placed in a thermostat at a temperature of 25° for forty-eight hours or longer, after which about 50 cc. of the solution was filtered into a weighed, glass-stoppered Erlenmeyer flask and the exact weight determined. The water was evaporated at about 80° and the residue dried to constant weight at a temperature of 120° to remove water of crystallization. Considerable difficulty was experienced in obtaining satisfactory checks, due possibly to the formation of different hydrates; the values given in Table II represent the average of several determinations in each case and express the order of magnitude of the solubilities.

TABLE II

SOLUBILITIES OF SODIUM SALTS OF SULFONYLIDE DERIVATIVES OF *m*-BENZENE DISULFONIC ACID

Sodium salt of	Soly., g. per 100 g. of water	Sodium salt of	Soly., g. per 100 g. of water
2-Hydroxy-5-methyl-[a]	0.75	5-Chloro-4-hydroxy-	0.58
4-Hydroxy-5-methyl-	0.61	6-Chloro-4-hydroxy-	0.89
5-Chloro-2-hydroxy-	1.6	(6-Hydroxy-*m*-toluene sulfonic acid) sulfonylide-5-sulfonic acid	.13

[a] Dried at 140°.

Summary

1. A satisfactory method has been described for the preparation in good yields of sulfonylides of the disulfonic acids of *p*-cresol, *o*-cresol, *p*-chlorophenol, *o*-chlorophenol and *m*-chlorophenol. A monosulfonic acid of (6-hydroxy-*m*-toluene sulfonic acid) sulfonylide has also been prepared and described.

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[9] Anschütz and Cürten, *Ann.*, **457**, 264 (1927).

2. The sulfonamides and the methyl esters of the sulfonylides of *p*-cresol disulfonic acid and of *o*-cresol disulfonic acid have been prepared. The molecular weights of the esters have furnished further proof of the bimolecular formula which has been assigned to the sulfonylides.
3. The approximate solubility of the sodium salt of each of the sulfonylides has been determined.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE ACTION OF CYCLOHEXYLMAGNESIUM BROMIDE ON DERIVATIVES OF OXALIC ACID

BY CHESTER G. GAUERKE[1] WITH C. S. MARVEL

RECEIVED DECEMBER 6, 1927 PUBLISHED APRIL 5, 1928

The reactions of various Grignard reagents on esters of oxalic acid have been studied by many different chemists. Valeur,[2] Bouvet[3] and Meerwein[4] have reported varying yields of tetra-alkyl ethylene glycols and of ethyl dialkyglycolates from the action of Grignard reagents on ethyl oxalate. Egorowa[5] and Wenus[6] have found that tertiary alkyl magnesium halides react with ethyl oxalate to give esters of the general formula, $R_3CCHOHCO_2C_2H_5$. Hepworth[7] has observed that by limiting the amount of the alkyl Grignard reagent used, the reaction can be confined to one of the ester groups and thus good yields of disubstituted glycolic esters can be obtained. On the other hand, Valeur[8] has observed that phenylmagnesium bromide reacts with methyl oxalate to give benzopinacol, $(C_6H_5)_2C(OH)C(OH)(C_6H_5)_2$, in very good yields.

In attempting to find a satisfactory method for the preparation of tetracyclohexyl ethylene glycol, $(C_6H_{11})_2C(OH)C(OH)(C_6H_{11})_2$, the reaction of cyclohexylmagnesium bromide and ethyl oxalate was studied. It was found that the main product of this reaction was ethyl dicyclohexylgycolate, $(C_6H_{11})_2C(OH)CO_2C_2H_5$. Only small amounts of the desired glycol were obtained even when a large excess of the Grignard reagent was used. By replacing ether, which is the common solvent for the Grignard

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[1] This communication is an abstract of a thesis submitted by Chester G. Gauerke in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Valeur, *Compt. rend.*, **132,** 833 (1901).

[3] Bouvet, *Bull. soc. chim.*, [4] **17,** 202 (footnote) (1915).

[4] Meerwein, *Ann.*, **419,** 151 (1919).

[5] Egorowa, *J. Russ. Phys.-Chem. Soc.*, **41,** 1454 (1909); *Chem. Zent.*, [I] **81,** 1003 (1910).

[6] Wenus, *J. Russ. Phys.-Chem. Soc.*, **46,** 1332 (1914); *Chem. Zent.*, [I] **86,** 1055 (1915).

[7] Hepworth, *J. Chem. Soc.*, **115,** 1203 (1919).

[8] Valeur, *Bull. soc. chim.*, [3] **29,** 684 (1903).