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).

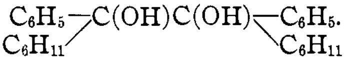
reaction, by benzene the yield of glycol was increased slightly. However, the reaction runs too poorly to be of use as a source for this compound. Two other esters of oxalic acid, namely methyl and *iso*propyl, were used in place of the ethyl ester, but the main products of the reactions were respectively the methyl and the *iso*propyl esters of dicyclohexylglycolic acid.

Oxalyl chloride was next used since it was expected that this would prove more reactive. This did yield traces of the desired glycol but the main reaction product was dicylohexyl ketone. This indicates that decomposition of oxalyl chloride or of some intermediate product must occur.

The failure of cyclohexylmagnesium bromide to produce the glycol in good yields, when the corresponding phenyl derivative works very well, is of considerable interest. It would be expected that the saturated ring would occupy a somewhat greater space and that steric hindrance effects would be more noticeable in cyclohexyl derivatives than in the corresponding phenyl compounds. However, it would hardly be expected that the difference in size between the saturated and the phenyl rings would be sufficient to stop the reaction at the hydroxy ester stage when the saturated ring is used.

If the reaction proceeds in the same stages when phenylmagnesium bromide reacts with an oxalate, an intermediate product would be an ester of benzilic acid, $(C_6H_5)_2C(OH)CO_2H$. It was thought that further information concerning the reactions could be obtained by studying the effects of various Grignard reagents on the esters of dicyclohexylglycolic acid and of benzilic acid.

It was found that ethyl dicyclohexylglycolate was recovered unchanged after prolonged action of cyclohexylmagnesium bromide, phenylmagnesium bromide or ethylmagnesium bromide. On the other hand, methyl benzilate reacts with an excess of cyclohexylmagnesium bromide to give a hydroxyketone, $(C_6H_5)_2C(OH)COC_6H_{11}$. The reaction apparently stops at this stage since none of the glycol could be obtained. With benzil, $C_6H_5COCOC_6H_5$, cyclohexylmagnesium bromide produces the glycol,



$\begin{matrix}C_6H_5\\C_6H_{11}\end{matrix}\!>\!C(OH)C(OH)\!<\!\begin{matrix}C_6H_5\\C_6H_{11}\end{matrix}$.

These observations are of interest in showing the marked difference in the behavior of the phenyl and cyclohexyl groups in these reactions. However, they are not of such a nature as to allow one to conclude whether the difference in the reactions is due to steric hindrance effects or to some activating influence of the phenyl groups on neighboring carbonyl groups.

In further attempting to obtain tetracyclohexyl ethylene glycol the reduction of dicyclohexyl ketone was studied. No greater success resulted with this reaction.

Experimental Part

Cyclohexylmagnesium Bromide and Ethyl Oxalate.—In a 2-liter, three-necked flask fitted with a stirrer, a reflux condenser and separatory funnel was placed 1.2 moles of cyclohexylmagnesium bromide (2 *N* solution in ether) and to it was added a solution of 32 g. (0.22 mole) of ethyl oxalate in 100 cc. of dry benzene during a period of two hours. When this addition was complete 1 liter of dry benzene was added and most of the ether was removed from the reaction mixture by distillation. The mixture was then stirred continuously and heated to gentle boiling for about four days until a test[9] for the Grignard reagent was negative. The reaction mixture was decomposed with dilute sulfuric acid in the usual way and the solvent was removed by distillation at ordinary pressure. The residue was distilled under reduced pressure and two main fractions were obtained.

The first of these boiled at 138–150° at 4 mm. and weighed 14 g. On standing it partially solidified and on crystallization from acetone yielded a white, crystalline solid, m. p. 69° (corr.). Analysis showed that this was ethyl dicyclohexylglycolate. This was also shown by hydrolysis and isolation of the acid.

Anal. Subs., 0.2004, 0.2028; CO_2, 0.5259, 0.5317; H_2O, 0.1866, 0.1887. Calcd. for $C_{16}H_{28}O_3$; C, 71.59; H, 10.52. Found: C, 71.59, 71.52; H, 10.42, 10.42.

Ten grams of the ester were boiled under reflux in a copper flask with an excess of 50% potassium hydroxide for about five days. On cooling and filtering the solution 4 g. of unchanged ester was recovered. On acidifying the solution dicyclohexyglycolic acid separated. It was purified by solution in alkali and reprecipitation. It melted at 171–172° (corr.) and gave a neutral equivalent of 239 instead of theoretical 240. The acid was decomposed by cold concd. sulfuric acid to give carbon monoxide, water and dicyclohexyl ketone. This was identified by converting to the oxime, m. p. 158–160°, which agrees with the melting point recorded in the literature.[10]

The second fraction obtained from the reaction of cyclohexylmagnesium bromide and ethyl oxalate boiled at 180–210° at 0.5–1 mm. pressure. It weighed 4–5 g. It solidified on standing and after recrystallization from acetone yielded about 0.5 g. of a white, crystalline solid, m. p. 151–152° (corr.). It analyzed correctly for tetracyclohexyl ethylene glycol.

Anal. Subs., 0.1000, 0.1007; CO_2, 0.2893, 0.2934; H_2O, 0.1069, 0.1057. Calcd. for $C_{26}H_{46}O_2$: C, 79.93; H, 11.87. Found: C, 78.93, 79.49; H, 11.96, 11.74.

The reaction of cyclohexylmagnesium bromide and ethyl oxalate in anhydrous ether was studied under a variety of conditions as to concentration of reacting substances and time of reaction without giving the desired glycol. Some dicyclohexyl was isolated. The yield of pure ethyl dicyclohexylglycolate was never greater than about 20% of the theoretical amount.

Cyclohexylmagnesium Bromide and Other Esters of Oxalic Acid.—One mole of cyclohexylmagnesium bromide and 25 g. (0.21 mole) of methyl oxalate in ether solution gave 14 g. of a product boiling at 135–160° at 4–5 mm. From this after two crystallizations from acetone 6 g. of pure methyl dicyclohexylglycolate, m. p. 48.5° (corr.), was obtained.

Anal. Subs., 0.1071; CO_2, 0.2766; H_2O, 0.0992. Calcd. for $C_{15}H_{26}O_3$: C, 70.81; H, 10.30. Found: C, 70.46; H, 10.36.

In a similar way 1.01 moles of cyclohexylmagnesium bromide and 30 g. (0.172 mole) of *iso*propyl oxalate gave 8.5 g. of a product boiling at 140–160° at 7 mm., from

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[9] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

[10] Zelinsky and Gawerdowskaja, *Ber.*, **60**, 714 (1927).

which after two crystallizations from acetone 4 g. of pure *iso*propyl dicyclohexylglycolate, m. p. 80° (corr.), was obtained.

Anal. Subs., 0.1325; CO_2, 0.3526; H_2O, 0.1260. Calcd. for $C_{17}H_{30}O_3$; C, 72.29; H, 10.71. Found: C, 72.60; H, 10.64.

Grignard Reagents and Ethyl Dicyclohexylglycolate.—Three solutions of ethyl dicyclohexylglycolate in dry benzene were treated with ether solutions of excess cyclohexylmagnesium bromide, phenylmagnesium bromide and ethylmagnesium bromide, respectively. The solutions were refluxed for long periods, but on working up the mixtures about 90% of the ester was recovered unchanged in each case.

Cyclohexylmagnesium Bromide and Methyl Benzilate.—To 0.73 of a mole of cyclohexylmagnesium bromide in 300 cc. of di-*n*-butyl ether,[11] in a 2-liter flask fitted with stirrer, reflux condenser and separatory funnel, was added 50 g. (0.2 mole) of methyl benzilate in 200 cc. of dry ether. The reaction mixture was stirred and gently boiled for about twenty-four hours until the test for the Grignard reagent was negative. An additional 0.12 of a mole of the Grignard reagent was added and the heating and stirring were continued for two days until the test for the Grignard reagent was again negative. The reaction mixture was worked up in the usual way and most of the di-*n*-butyl ether was removed by distillation under reduced pressure. The residue (about 150 cc.) was cooled overnight at −10° and a solid separated. The solid was collected on a filter. From the mother liquors a second crop of crystals was obtained. The product was recrystallized from ligroin and 23 g. of pure crystals, m. p. 112.5° (corr.), was obtained. Analysis showed that this product was the hydroxy ketone, $(C_6H_5)_2C(OH)COC_6H_{11}$.

Anal. Subs., 0.1158, 0.1060; CO_2, 0.3468, 0.3171; H_2O, 0.0781, 0.0718. Calcd. for $C_{20}H_{22}O_2$: C, 81.59; H, 7.53. Found: C, 81.70, 81.61; H, 7.54, 7.57.

A sample of this product was boiled with alcoholic potassium hydroxide and was thus decomposed into the potassium salt of hexahydrobenzoic acid and diphenyl carbinol. Phenylbenzoin decomposes in a like manner to give potassium benzoate and diphenyl carbinol.[12]

When ethyl ether was used as the solvent, only small amounts of the hydroxy ketone were obtained.

Cyclohexylmagnesium Bromide and Benzil.—To 0.4 of a mole of cyclohexylmagnesium bromide in 215 cc. of ether was added 44 g. (0.21 mole) of benzil in 250 cc. of ether over a period of four hours. The reaction mixture was stirred at room temperature for about eight hours until the test for the Grignard reagent was negative. Then an additional 0.5 of a mole of the Grignard reagent was added and the solution was stirred and refluxed for about six hours. After decomposing the reaction mixture in the usual way, the ether layer was separated and evaporated. On standing a solid separated from the residue and the mixture was filtered with suction. The filtrate was steam distilled and another crop of crystals was filtered from the solution left behind. On recrystallizing the solid from ether 8 g. of a product, m. p. 150–151° (corr.), was obtained. Analysis showed that the product was the expected symmetrical diphenyl dicyclohexyl ethylene glycol.

Anal. Subs., 0.1375; CO_2, 0.4172; H_2O, 0.1124. Calcd. for $C_{26}H_{34}O_2$: C, 82.48; H, 9.06. Found: C, 82.78; H, 9.14.

Attempts to Prepare Tetracyclohexyl Ethylene Glycol by the Reduction of Dicyclohexyl Ketone.—Dicyclohexyl ketone was prepared from cyclohexylmagnesium bromide and hexahydrobenzoyl chloride according to the method of Johnson and Daw-

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[11] The use of di-*n*-butyl ether as a solvent for the Grignard reaction has been investigated in this Laboratory and will be discussed in detail in another paper.

[12] Nef, *Ann.*, **308**, 291 (1899).

son.[13] When this ketone was treated with magnesium and iodine according to the method of Gomberg and Bachmann,[14] it was recovered unchanged. Magnesium amalgam in benzene followed by water did not cause reduction. Sodium and alcohol reduced the ketone to give a 76% yield of dicyclohexyl carbinol.

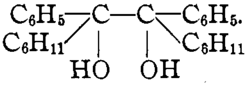
Summary

1. Cyclohexylmagnesium bromide reacts with esters of oxalic acid to give as the main product the corresponding ester of dicyclohexylglycolic acid. Small amounts of tetracyclohexyl ethylene glycol can be obtained.

2. Ethyl dicyclohexylglycolate does not react readily with either ethylmagnesium bromide, phenylmagnesium bromide or cyclohexylmagnesium bromide.

3. Methyl benzilate reacts with cyclohexylmagnesium bromide to give an hydroxy ketone, $(C_6H_5)_2C(OH)COC_6H_{11}$.

4. Benzil reacts with cyclohexylmagnesium bromide to give the symmetrical diphenyl dicyclohexyl ethylene glycol,



$$(C_6H_5)(C_6H_{11})C(OH)\text{—}C(OH)(C_6H_5)(C_6H_{11}).$$

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ST. STEPHEN'S COLLEGE]

ORGANIC SELENIUM COMPOUNDS. SOME DERIVATIVES OF AROMATIC SELENO-ETHERS

BY DUNCAN GRAHAM FOSTER AND STANLEY F. BROWN

RECEIVED DECEMBER 6, 1927 PUBLISHED APRIL 5, 1928

Introductory

The researches reported in this paper originated in an attempt to duplicate, with compounds containing selenium, certain investigations conducted by Reid, with the senior author of this paper,[1] and with other investigators,[2,3] upon the influence of a sulfur atom in varying positions in the molecule on the color of a series of azo dyes. It had been our intention to employ exactly analogous methods to those outlined in references (1) and (2) in order to prepare nitro seleno-ethers, $O_2NC_6H_4SeR$, and from them amino seleno-ethers of the type, $H_2NC_6H_4SeR$, which could be diazotized and coupled with standard intermediates to give azo dyes.

These methods were found to be completely unfruitful because of the instability of the *o*- and *p*-nitroselenophenols, $O_2NC_6H_4SeH$, which oxidize

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[13] Private communication.

[14] Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

[1] Foster and Reid, THIS JOURNAL, **46**, 1936 (1924).

[2] Waldron and Reid, *ibid.*, **45**, 2399 (1923).

[3] Palmer and Reid, *ibid.*, **48**, 528 (1926).