Dichloromercuridimethoxyphenylbutane.—A solution of 0.4 g. (0.001 mole) of chloromercurimethoxyphenylbutene in 5 cc. of methanol was treated with 0.32 g. (0.001 mole) of mercuric acetate. The latter dissolved immediately but test portions gave a precipitate with 10% aqueous sodium hydroxide for twelve hours. After thirty-six hours a solution of 10% sodium chloride was added. The precipitated solid melted roughly at 100°. After washing with hot ethanol it melted at 180° and weighed 0.16 g. The compound can be obtained more easily by treating the diacetoxymercuridimethoxyphenylbutane in methanol with exactly two equivalents of dilute hydrochloric acid. The compound crystallizes slowly from acetone.

Anal. Calcd. for $C_{12}H_{16}O_2Hg_2Cl_2$: C, 21.68; H, 2.43. Found: C, 21.60; H, 2.52.

Summary

1. The rate of mercuration of ethylenes has been found to depend on a bimolecular reaction.

2. Some *cis* ethylenes mercurate more rapidly than the *trans* isomers.

3. An alternative mechanism is suggested to explain the mercuration.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VASSAR COLLEGE]

The Reaction between 2,3-Dimethyl-1,4-naphthoquinone and Phenylmagnesium Bromide.[1] I

BY H. MARJORIE CRAWFORD

Numerous studies have been made of the reactions between quinones and Grignard reagents. Only in the cases of anthraquinone[2] and phenanthraquinone[3] were the reactions clean-cut and the yields good. The mono- or di-addition product resulted, depending on the relative amounts of reactants.

If there was a possibility of a 1,4 addition to a conjugated system besides the addition to the carbonyl group, the reactions were complicated, many different products resulted and tars and oils formed the main products of the reaction. Bamberger[4] studied the reaction of methylmagnesium iodide on *p*-xyloquinone and identified six solid products which accounted for only one-fourth of the quinone used. Another fourth was reduced to the hydroquinone, and amorphous solids and oils remained. Franssen,[5] using α-naphthoquinone, isolated a di-addition product in 25% yields, but obtained colored amorphous products, reduction products and tars. Thinking that these complex results might have been due to hydrogen atoms attached to the quinone nucleus, Smith and Crawford[6] studied the reaction between a fully substituted quinone (duroquinone) and phenylmagnesium bromide and found that in this case also the reaction was very complex. The main product of the reaction was an oil (80%) and from the other 20% eight solids were separated and identified. 1,2- and 1,4-addition occurred as well as reduction and the formation of double compounds of the quinhydrone type.

Discussion of the Reaction and Products

In the present work, 2,3-dimethyl-1,4-naphthoquinone was chosen because it appeared to be intermediate in structure between duroquinone, which gave complex results, and anthraquinone which gave clean-cut results. However, it seems that as long as any 1,4-conjugated system is open the reaction is complicated, even though one side of the quinone is blocked by a benzene ring. The predicted mono- and di-addition products were obtained as well as double compounds, reduction products and dehydration products.

Three types of reaction products were formed and will be discussed separately, although all were formed at the same time. If one or one and a half moles of phenylmagnesium bromide was used per mole of the quinone, mono- and di-addition products were formed. If two moles of phenylmagnesium bromide were used per mole of quinone, di-addition products predominated.

A. Reduction Products.—The reduction of quinones by Grignard reagents is quite general and, regardless of procedure, reduction products

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[1] Presented in part at the New York meeting of the American Chemical Society in April, 1935.

[2] (a) Haller and Guyot, *Compt. rend.*, **138**, 327 and 1251 (1904); (b) Guyot and Staehling, *Bull. soc. chim.*, **33**, 1104 and 1144 (1905); (c) Haller and Comtesse, *Compt. rend.*, **150**, 1290 (1910); (d) Clarke and Carleton, THIS JOURNAL, **33**, 1966 (1911).

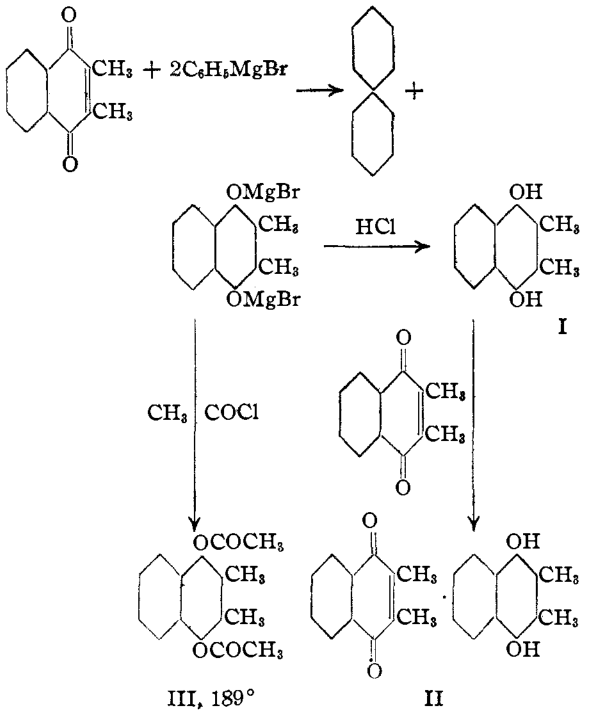
[3] (a) Werner and Grob, *Ber.*, **37**, 2887 (1904); (b) Zincke and Tropp, *Ann.*, **362**, 242 (1908); (c) Bachmann and Chu, THIS JOURNAL, **57**, 1095 (1935).

[4] Bamberger, *Ann.*, **384**, 272 (1911).

[5] Franssen, *Bull. soc. chim.*, **37**, 902 (1925); **45**, 1030 (1929).

[6] Smith and Crawford, THIS JOURNAL, **50**, 869 (1928).

were obtained corresponding to about 10% of the quinone.

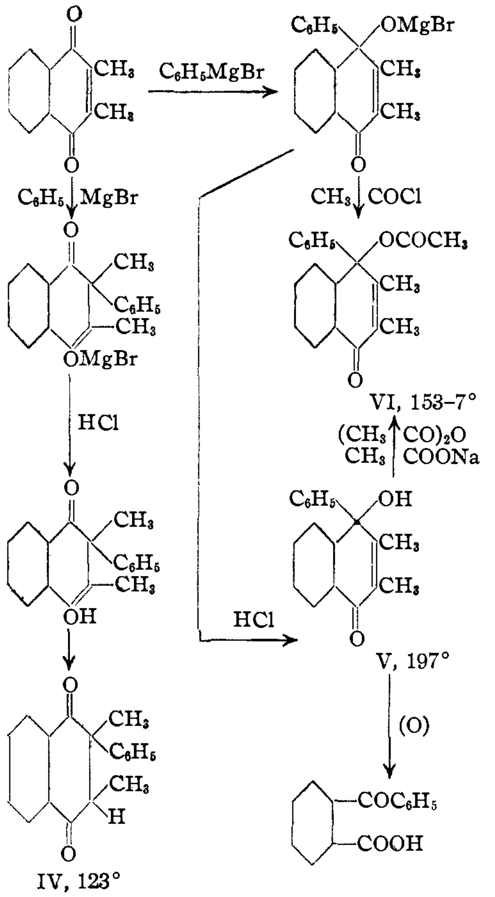


The diacetate of the hydroquinone (III) was obtained when the green reaction mixture was decomposed by acetyl chloride. The hydroquinone (I) was formed when the reaction mixture was decomposed by ice and hydrochloric acid. It was isolated as the quinhydrone (II), a black solid.

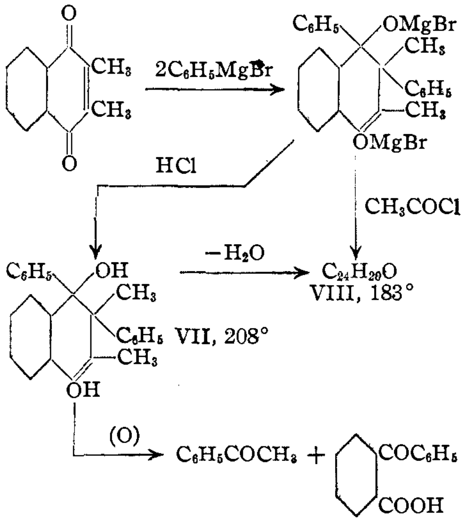
B. Mono-addition Products.—One molecule of phenylmagnesium bromide may react with one molecule of the quinone to give either a 1,2 or a 1,4 addition product (see next diagram).

The 123° compound (IV) was obtained in small amounts in two runs. Oxidation to give acetophenone indicates a 1,4 addition. The keto structure is more probable than the enol first formed, for the Grignard machine[7] shows no active hydrogen.

The 197° compound (V) had one active hydrogen and one carbonyl group (Grignard machine), and on oxidation gave *o*-benzoylbenzoic acid. The 197° compound was obtained in all reactions, and accounts for about one-fourth of the solid products isolated. The corresponding 153–157° acetate (VI) was obtained once when the reaction mixture was decomposed by acetyl chloride.



C. Di-addition Products.—The main solid product in most reactions was the 208° compound (VII)



Its structure was established by analyses, by the fact that the Grignard machine showed two active hydrogens and no carbonyl group, and by oxidation to acetophenone and *o*-benzoylbenzoic acid.

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[7] Kohler and co-workers, THIS JOURNAL, 49, 3181 (1927); 52, 3736 (1930).

The nature of the 183° compound (VIII) is under investigation. It corresponds to a di-addition product minus one molecule of water, and is obtained by treating the metallic addition product with acetyl chloride, or from the 208° compound by reagents which suggest a pinacol rearrangement.

Another di-addition product (IX) melting at 203° was obtained in very small amounts (less than 0.5 g.). It was isolated from the reaction mixture in the form of a double compound (X) containing two molecules of quinone to one molecule of the 203° compound.

$$\underset{\text{IX, }203°}{C_{24}H_{22}O_2} + 2C_{12}H_{10}O_2 \rightleftarrows \underset{\text{X, }137°}{C_{24}H_{22}O_2 \cdot 2C_{12}H_{10}O_2}$$

There is also a dehydration product, $C_{24}H_{20}O$, (XI) related in some way to the 203° compound (IX). These products are being further investigated.

Total yields of solid products from 348 g. of quinone (1.87 mole) and 3.5 moles of phenylmagnesium bromide: quinone and quinhydrone, 65 g.; 208° compound, 40 g.; 197° compound, 20 g.; 123° compound, 2.4 g.; 137° compound, 14 g.

Total yields of solid products from 55.8 g. of quinone (0.3 mole) and 0.55 mole of phenylmagnesium bromide when the reaction mixture was decomposed by excess acetyl chloride: quinone, 7.6 g.; 153° acetate, 0.22 g.; 189° diacetate, 7.9 g.; 183° compound, 1.1 g.

Experimental Part

All combustions were carried out using the semi-micro method of Lauer and Dobrovolny.[8] Molecular weight determinations were made by the lowering of the freezing point of benzene, or by the Rast method using camphor as the solvent.

Preparation of the 2,3-Dimethyl-1,4-naphthoquinone.—The quinone was prepared from 2,3-dimethylnaphthalene according to the method of Kruber[9] in 41–48% yields, m. p. 125–127°. Variations in the procedure, including lower temperatures and the use of a stirrer, did not affect the yield. Glacial acetic acid was the best solvent for recrystallization.

The Reaction between 2,3-Dimethyl-1,4-naphthoquinone and Phenylmagnesium Bromide.—Reactions carried out as nearly alike as possible gave different results, and for this reason the quinone was divided into small amounts and the reaction products worked up separately. One, one and a half or two moles of phenylmagnesium bromide were used per mole of quinone.

A freshly prepared Grignard solution containing approximately 0.1 mole of phenylmagnesium bromide per 100 cc. was added slowly to a suspension of 18.6 g. (0.1 mole) of 2,3-dimethyl-1,4-naphthoquinone in ether. The solid addition product was bright green. The mixtures were allowed to stand overnight before decomposing with ice and hydrochloric acid. The water layer, colored bright purple by quinhydrone, was extracted with ether. The ether solutions, after evaporating to about 50 cc., were diluted to 100 cc. with diisopropyl ether. Crops of solid obtained on standing were filtered off and washed with diisopropyl ether. Similar crops were combined for crystallization. In every case a dark oil was the main product.

In three cases the first green magnesium addition products, after standing for four hours, were decomposed with excess acetyl chloride and allowed to stand overnight, then treated with ice and hydrochloric acid. The yields in these cases were small and the acetates hard to isolate. The main product was the diacetate of the hydroquinone. The 153–157° acetate (VI) and the 183° compound (VIII) were obtained in small amounts.

Diphenyl could always be obtained by steam distillation of the oils, or from the ether filtrate if the original green magnesium compound was removed by filtration.

In one case the quinone was added to the Grignard reagent and the green precipitate first formed dissolved to give a yellowish brown solution. The yield of solids was low.

The Hydroquinone, I.—The hydroquinone was isolated in practically every reaction as the black quinhydrone.

It was also prepared from the quinone by reduction with boiling 80% acetic acid and excess zinc dust. The solution turned dark red at first, but in twenty minutes was practically colorless. A white precipitate formed as soon as the filtered solution cooled, but all attempts to filter, wash and dry it, even in an atmosphere of nitrogen, resulted in color changes from white through pink, lavender and purple, to black. The melting point is around 135–140° but no very definite results could be obtained due to its extreme ease of oxidation.

The Quinhydrone, II, m. p. 136–140°.—This substance was obtained in most of the reactions. It could be recrystallized from alcohol or ether and separated from the dark red solution as glistening black leaflets. Considerable oxidation to quinone occurred unless the recrystallization was carried out rapidly.

Anal. Calcd. for $C_{24}H_{22}O_4$: C, 76.97; H, 5.93. Found: C, 76.21, 76.87; H, 5.93, 6.17.

The compound dissociates in solution and while the quinone is very soluble in benzene, the hydroquinone is not so soluble. This gave a high result for the molecular weight, 224 instead of 187.

Diacetate of the Hydroquinone, III, m. p. 189–189.5°.—This diacetate was formed when the solid magnesium addition product was treated with acetyl chloride. It was also made by boiling the quinone with acetic anhydride and zinc dust, and from the impure hydroquinone by treatment with phenylmagnesium bromide followed by acetyl chloride. It is white when pure, and is soluble in chloroform but only slightly soluble in alcohol and benzene.

Anal. Calcd. for $C_{16}H_{16}O_4$ (272.1): C, 70.55; H, 5.92.

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[8] Lauer and Dobrovolny, *Mikrochem. Pregl Festschr.*, 243 (1929).

[9] Kruber, *Ber.*, **62**, 3044 (1929).

Found: C, 70.22, 70.20, 70.15; H, 5.92, 5.74, 5.71; mol. wt. (camphor), 284.4.

1,4 - Dioxo - 2,3 - dimethyl - 2 - phenyltetrahydronaphthalene, IV, m. p. 123°.—This mono-addition product was obtained in very small yields in two runs: 2.4 g. from 348 g. of quinone. It is a white solid, quite soluble in alcohol, ether and benzene. Half a gram was boiled for five hours with 2 g. of potassium dichromate in 15 cc. of acetic acid. An ether extract of the neutralized oxidation mixture was treated with semicarbazide, and gave acetophenonesemicarbazone.

Anal. Calcd. for $C_{18}H_{16}O_2$ (264.1): C, 81.78; H, 6.11. Found: C, 81.19, 81.04; H, 6.07, 5.99; mol. wt. (benzene), 257.3, 256.4.

1 - Oxy - 4 - oxo - 2,3 - dimethyl - 1-phenyldihydronaphthalene, V, m. p. 197–197.5°.—This compound is formed in practically all reactions. It is a white solid soluble in pyridine, 1,4-dioxane, chloroform and ether, but only slightly soluble in alcohol and benzene, and practically insoluble in diisopropyl ether. A mixture of chloroform and alcohol was best for crystallization. Phosphorus tribromide in bromoform solution gave a red brown oil. A solution of 1 g. of the 197° compound and 0.7 g. of hydroxylamine hydrochloride in 50 cc. of pyridine heated on the steam-bath for twelve hours gave 0.95 g. of the starting material unchanged.

Anal. Calcd. for $C_{18}H_{16}O_2$ (264.1): C, 81.78; H, 6.11. Found: C, 81.57, 81.68, 81.65; H, 6.20, 6.17, 6.24; mol. wt. (camphor), 265.6, 280.3.

The Grignard machine showed 1.12 moles of methane liberated and 1.86 moles of methylmagnesium iodide reacting per mole of 197° compound.

Oxidation.—One gram of the 197° compound and 3 g. of potassium dichromate in 25 cc. of glacial acetic acid were boiled for six hours. The mixture was then diluted with 100 cc. of water, neutralized with sodium carbonate and extracted with ether. An ether extract of the acidified water layer gave *o*-benzoylbenzoic acid melting at 126–128°.

Treatment of the 197° compound with sodium followed by acetyl chloride, and heating with acetyl chloride alone failed to give the acetate.

Acetate of 1-Oxy-4-oxo-2,3-dimethyl-1-phenyldihydronaphthalene, VI, m. p. 153–157°.—A mixture of 1.6 g. of the 197° compound, 2 g. of fused sodium acetate and 30 cc. of freshly distilled acetic anhydride was boiled for four hours. After cooling, water was added to dissolve the sodium acetate, the layers were separated and the water layer discarded. After the addition of alcohol and the evaporation of the solvents, 0.73 g. of the very soluble acetate separated.

This acetate was also obtained once (0.22 g.) when the original green metallic addition product was decomposed by acetyl chloride. It is very soluble in alcohol, ether, ethyl acetate and diisopropyl ether, and crystallizes in needles.

Anal. Calcd. for $C_{20}H_{18}O_3$: C, 78.39; H, 5.92. Found: C, 78.53, 77.90, 78.15; H, 5.80, 5.98, 6.00.

1,4 - Dioxy - 2,3 - dimethyl - 1,2 - diphenyldihydronaphthalene, VII, m. p. 208–209°.—This compound was formed in larger amounts than any of the other addition products. It is a white solid, soluble in ethyl acetate, pyridine, 1,4-dioxane and chloroform, but only slightly soluble in alcohol, benzene and ethers (diethyl, diisopropyl and diisoamyl). The best solvents for recrystallization are ethyl acetate or a mixture of alcohol and chloroform. From the reaction mixture the 208° compound and the 197° compound (V) often separate together as an apparently homogeneous material melting at 175°. Separation could be effected by dissolving the 175° material in boiling chloroform, then adding diisopropyl ether. The first solid separating was mainly the 197° compound. The middle fractions melted at 175°, and the final fractions were mainly the 208° compound.

Anal. Calcd. for $C_{24}H_{22}O_2$ (342.2): C, 84.17; H, 6.48, Found: C, 83.93, 84.04, 83.86; H, 6.56, 6.55, 6.51; mol. wt. (camphor), 347.8.

The Grignard machine showed 1.6, 1.7, 1.8 moles of methane per mole of the 208° compound. The gas was shown to be methane by analysis. The slight solubility of the 208° compound in solvents inert to the methylmagnesium iodide prevented further reaction.

Oxidation.—Two grams of the 208° compound and 6 g. of potassium dichromate in 50 cc. of glacial acetic acid were heated under reflux for five hours, then cooled and diluted with 200 cc. of water. The solution was neutralized with potassium hydroxide and extracted with ether. The ether solution, on treatment with semicarbazide, gave acetophenonesemicarbazone. The water solution was acidified with sulfuric acid and extracted with ether. The white solid, melting 126–128° was shown to be *o*-benzoylbenzoic acid by conversion to anthraquinone and mixed melting point with a known sample of anthraquinone.

Potassium permanganate in acetone failed to oxidize the 208° compound. When 1 g. of the 208° compound was heated for twelve hours on the steam-bath with hydroxylamine hydrochloride in pyridine solution, 0.63 g. was recovered unchanged, and 0.5 g. of an oil remained.

In an attempt to make the acetate by adding acetyl chloride to the magnesium derivative resulting from the reaction of the 208° compound with Grignard reagent, a white solid was obtained which melted at 183° (VIII). Treatment of the 208° compound with phosphorus tribromide in bromoform solution gave the same 183° compound. Heating 1 g. of the 208° compound on the steam-bath for six hours with zinc chloride and hydrochloric acid in benzene, or heating 1 g. for an hour with 0.5 g. of iodine in 50 cc. of acetic acid gave practically quantitative conversion to the 183° compound. This latter method was the procedure followed by Bachmann and Chu[3c] in rearranging their 9,10-diaryldihydrophenanthrenediols to diarylphenanthrones. Heating the 208° compound with 20% sulfuric acid for one half hour caused no loss of water.

$C_{24}H_{20}O$, VIII, m. p. 183°.—This compound results when the 208° compound loses a molecule of water. It was also formed when the original green reaction mixture was treated with acetyl chloride. After separating the diacetate of the hydroquinone, the remaining oils were distilled under reduced pressure. The fraction boiling 250–270° (15 mm.) finally gave 1.1 g. of the 183° compound from 70.4 g. of oil.

This compound is very soluble in alcohol, ether and benzene and separates in shining white leaflets. Heating 0.5 g. of the 183° compound with 20 cc. of constant boiling hydrobromic acid for three hours gave 0.4 g. of unchanged material. The starting material was recovered unchanged after heating on the steam-bath for seven hours with hydroxylamine. After heating 1 g. for five hours with potassium dichromate at the boiling point of acetic acid, 0.75 g. of the 183° compound was recovered unchanged.

Anal. Calcd. for $C_{24}H_{20}O$ (324.2): C, 88.84; H, 6.22. Found: C, 88.81, 88.87; H, 6.42, 6.22; mol. wt. (benzene), 315.1, 329.1.

The Grignard machine showed no active hydrogen, but 1.05 mole of methylmagnesium iodide reacted per mole of the 183° compound.

$C_{24}H_{22}O_2$, **IX**, m. p. 203–204°.—This white di-addition product was very soluble in benzene and alcohol, and was obtained from the reaction mixture in the form of a double compound (X) with two molecules of quinone. The clear crystals first obtained soon became opaque and sticky even in a desiccator. Less than 0.5 g. was available for study and the oxidation of 0.2 g. of this was inconclusive, so no structure can be assigned at this time.

Anal. Calcd. for $C_{24}H_{22}O_2$ (342.2): C, 84.17; H, 6.48. Found: C, 84.86, 83.75, 83.70; H, 6.66, 6.44, 6.46; mol. wt. (benzene), 338.8.

$C_{24}H_{22}O_2 \cdot 2C_{12}H_{10}O_2$, **X**, m. p. 137–138°.—The thick prisms of this yellow compound separated from various reaction mixtures and could be recrystallized from diisopropyl ether. Recrystallization from alcohol gave first quinone, then 137° compound, and finally the very soluble white di-addition product (IX). When the white compound (IX) and quinone were recrystallized together from alcohol, the yellow 137° compound was formed. The quinone could also be separated from the white compound by steam distillation.

Anal. Calcd. for $C_{24}H_{22}O_2 \cdot 2C_{12}H_{10}O_2$ ($[342 + 2(186)]/3 = 238$): C, 80.63; H, 5.93. Found: C, 79.66, 79.56; H, 5.96, 5.80; mol. wt. (benzene), 226.2.

$C_{24}H_{20}O$, **XI**, m. p. 124°.—This dehydration product is related in some way to the 203° compound (IX), and was obtained only once (2.15 g.) out of fifteen runs. The structure is still under investigation. Oxidation with potassium dichromate gave acetophenone and *o*-benzoylbenzoic acid.

Anal. Calcd. for $C_{24}H_{20}O$ (324.2): C, 88.84; H, 6.22. Found: C, 88.98, 88.64; H, 6.22, 6.40; mol. wt. (benzene), 316.5, 314.9.

The Grignard machine showed no active hydrogen, but 0.7 mole of methylmagnesium iodide reacted per mole of the 124° compound.

The author wishes to thank Lillian G. Hoagland, formerly instructor at Vassar College, for much preliminary work on other methods of preparing the quinone, and for the preparation of the hydroquinone and its diacetate.

Summary

1. Whenever a 1,4-conjugated system in a quinone is open to attack by a Grignard reagent the reaction is complex and the yields of solids low.

2. A study of the reaction between 2,3-dimethyl-1,4-naphthoquinone and phenylmagnesium bromide shows that several reactions take place at the same time and the quinone acts more like duroquinone than like anthraquinone.

3. Eleven new compounds, products of this reaction and their derivatives, are described and structures are proposed for seven of them. About 70% of the reaction product is a dark oil.

4. The study of the dehydration products is being continued.

POUGHKEEPSIE, N. Y. RECEIVED JULY 12, 1935