as just described above for benzylidene aniline, benzylidene *p*-toluidine forms a compound which melts at 136–137° when recrystallized from alcohol. The crystals thus obtained are much more difficult to purify than those obtained from benzylidene aniline. Furthermore, they are very easily converted into benzyl *p*-tolylbenzamidine, this reaction taking place when less than one molecular equivalent of potassium amide is present in the ammonia solution.

Anal. Calcd. for $C_{35}H_{33}N_3$: C, 84.8; H, 6.7. Found: C, 84.6, 84.3; H, 6.7, 6.3. *Mol. wt.* Calcd. for $C_{35}H_{33}N_3$: 495. Found: 399, 401.

It is with the greatest pleasure that the writer takes this opportunity to express his thanks to Dr. E. C. Franklin for the care which he exercised in directing the experimental work and in reading this manuscript.

Summary

Experimental evidence has been presented to show that the aromatic Schiff's bases, benzylidene aniline and benzylidene *p*-toluidine, are aldehyde-acetals of the ammonia system of compounds.

The ammonolysis of ammono aldehyde-acetals has been accomplished. Benzylphenylbenzamidine and benzyl-*p*-tolylbenzamidine have been prepared by the Cannizzaro reaction.

Benzoin-anil-anilide and benzoin-*p*-tolyl-*p*-toluide have been prepared by the benzoin condensation.

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THE REACTION BETWEEN ORGANOMAGNESIUM HALIDES AND ALKYL SULFONATES

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Introduction

Alkyl esters of sulfonic acids differ from aryl esters of sulfonic acids in their reaction with organomagnesium halides. With alkyl esters, alkylation takes place, and this reaction has generally been formulated as follows[1]

$$2RSO_2O\text{-Alkyl} + 2R'MgX \longrightarrow 2R'\text{-Alkyl} + (RSO_2O)_2Mg + MgX_2 \qquad (1)$$

With aryl esters, sulfones and phenols are formed, as follows

$$RSO_2\text{-OAryl} + R'MgX \longrightarrow RSO_2R' + \text{ArylOMgX} \qquad (2)$$

When molecular equivalents of alkyl sulfonate and Grignard reagent are used, according to Reaction 1, the yield of alkylation product does not generally exceed 50%.[2] This prompted a further investigation of the

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[1] Gilman, Robinson and Beaber, THIS JOURNAL, **48**, 2715 (1926). References to earlier studies are contained in this paper.

[2] Gilman and Beaber, *ibid.*, **47**, 518 (1925). The only exception to the 18 alkylation reactions reported by them was in the reaction between benzyl *p*-toluenesulfonate and benzylmagnesium chloride. In this case a 55% yield of dibenzyl was obtained, but it is quite probable that part of this high yield is due to some dibenzyl that is generally

reaction. The results described here show that Reaction 1 is only partly correct. In addition to the alkylation product an alkyl halide is formed, the alkyl group coming from the ester and the halogen from the Grignard reagent.

The following reactions are proposed to account for the formation of these compounds.

$$RSO_2O\text{-}Alkyl + R'MgX \longrightarrow R'\text{-}Alkyl + RSO_2OMgX \qquad (3)$$

$$RSO_2OMgX + RSO_2O\text{-}Alkyl \longrightarrow Alkyl\ X + (RSO_2O)_2Mg \qquad (4)$$

In strict accordance with these reactions the yield of alkylation product should be increased when two moles of alkyl sulfonate are used with one mole of Grignard reagent. This is supported by experiment. Also it has been shown that when two moles of ester are used for one of RMgX compound, the R-Alkyl and RX compounds are formed in essentially equivalent quantities. It is obvious that after some RSO_2OMgX has been formed according to Reaction 3, this salt would react with ester to give the RX compound according to Reaction 4 even when equivalent molecular quantities of ester and Grignard reagent are used. This, too, has been found to be the case.

The correctness of Reaction 4 has been established by treating anhydrous β-naphthalene sulfonic acid with methylmagnesium iodide to form β-$C_{10}H_7SO_2OMgI$, and then treating this salt with *n*-butyl *p*-toluenesulfonate to form *n*-butyl iodide and magnesium β-naphthalenesulfonate, as follows

$$\beta\text{-}C_{10}H_7SO_2OH + CH_3MgI \longrightarrow \beta\text{-}C_{10}H_7SO_2OMgI + CH_4 \qquad (5)$$

$$\beta\text{-}C_{10}H_7SO_2OMgI + p\text{-}CH_3C_6H_4SO_2OC_4H_9\ (n) \longrightarrow n\text{-}C_4H_9I + (\beta\text{-}C_{10}H_7SO_2O)_2Mg \qquad (6)$$

Kenyon, Phillips and Turley[3] obtained ethyl α-bromopropionate and not ethyl α-phenylpropionate (as might have been expected in accordance with Reaction 1) when the *p*-toluenesulfonic ester of optically active ethyl lactate was treated with phenylmagnesium bromide. Also, Rossander and Marvel,[4] in a study of the lengthening of carbon chains by three carbon atoms wherein γ-chloropropyl *p*-toluenesulfonate was treated with various RMgX compounds, obtained not only the normal reaction[5] leading to the introduction of the chloropropyl group but also the dihalide formed from the γ-chloropropyl group and the halogen of the Grignard reagent.

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formed in significant quantities in the preparation of benzylmagnesium chloride. Two other yields in excess of 50% have been reported by Gilman and Beaber with halogen alkyl sulfonates, *ibid.*, **45**, 839 (1923). The high yields obtained with dialkyl sulfates may be due to the presence of two alkyl groups in these esters in contrast with the one alkyl group in alkyl *p*-toluenesulfonates.

[3] Kenyon, Phillips and Turley, *J. Chem. Soc.*, **127**, 399 (1925). They also obtained ethyl α-bromopropionate from the lactyl ester and ethylmagnesium bromide. With ethoxymagnesium iodide (C_2H_5OMgI) and the lactyl ester they got ethyl α-iodopropionate. No other products from these three reactions were reported by them.

[4] Rossander and Marvel, THIS JOURNAL, **50**, 1491 (1928).

[5] Gilman and Beaber, *ibid.*, **45**, 839 (1923).

In some of their reactions where one mole of ester was used with one mole of Grignard reagent, they obtained significant quantities of the hydrocarbon that would be expected from the hydrolysis of the RMgX compound. An explanation for the formation of these hydrocarbons is to be found in Reactions 3 and 4. From these reactions it will be noted that the ester is competing for the RMgX and the RSO_2OMgX compounds, and inasmuch as these reactions probably take place concurrently (R-alkyl and RX are both formed from one mole of ester and one mole of RMgX) some of the RMgX compound will remain unused. This unused Grignard reagent would then give the corresponding hydrocarbon when the reaction mixture is subsequently hydrolyzed in the course of working up the reaction products.

In connection with the formation of hydrocarbon when equimolecular proportions of ester and Grignard reagents are used,[6] it is possible to formulate other reactions to account for the alkylation product and the alkyl halide. Kenyon, Phillips and Turley, and Holmberg[7] have proposed the following reaction to account for the formation of the ethyl α-bromopropionate

$$RSO_2O\text{–Alkyl} + R'MgX \longrightarrow \text{Alkyl X} + RSO_2OMgR'. \qquad (7)$$

Unless this reaction is peculiar to the lactyl ester of *p*-toluenesulfonic acid, and there is no reason at present to believe so in view of the several diverse alkylations that have been reported,[2] it should account for general alkylations involving the Grignard reagent. Their scheme of Reaction (7) accounts for the formation of alkyl halide; it can also explain the formation of hydrocarbon observed in some cases by Rossander and Marvel[4,6]; but it offers no satisfactory explanation for the alkylation action that is so common with alkyl sulfonates. It can account for the formation of hydrocarbon, because the RSO_2OMgR' compound postulated there has the highly reactive –MgR′ group that should show many, if not all, of the reactions of RMgX compounds. Hydrolysis of it, for example, should yield the hydrocarbon R′H.

A series of reactions has been proposed,[4] independently of the formulation just considered, to account for all of the products so far obtained in the reaction between alkyl sulfonates and RMgX compounds. This scheme admits Reaction 3 to account for a part of the alkylation; it admits Reaction 7 to account for the alkyl halide, and then with Reaction 7 as a basis it accounts for the formation of the remainder of the alkylation product and the hydrocarbon by the following reactions that assume the intermediate formation of RSO_2OMgR'

$$RSO_2O\text{–Alkyl} + RSO_2OMgR' \longrightarrow R'\text{–Alkyl} + (RSO_2O)_2Mg \qquad (8)$$

$$RSO_2OMgR' + HOH \longrightarrow R'H + RSO_2OMgOH \qquad (9)$$

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[6] When Marvel and Rossander (ref. 4) used two moles of ester with one of Grignard reagent they isolated a hydrocarbon in only one experiment.

[7] Holmberg, *Ber.*, **59**, 1560 (1926).

Admittedly this series of Reactions (3, 7, 8 and 9) offers not only an explanation for all of the products so far observed, but also accounts for the improvement of yield in the alkylation reaction when two moles of ester are used for one mole of Grignard reagent. There are, however, some objections to such a scheme of reactions. First, it calls for a manner of scission of the RMgX molecule that is unusual. Grignard reactions generally have been explained as involving, at some stage, a scission or dissociation of the molecule to give R– and –MgX and not RMg– and –X. Second, Reactions 7, 8 and 9 postulate a compound (RSO_2OMgR') which is unknown, so that it is impossible at present to verify these three reactions by the use of the RSO_2OMgR' compound about which all three reactions turn. Over and against such a proposal that has no confirmation in experiment is Reaction 4, which has found support in experiment. Reactions 3 and 4 account for (1) alkylation, (2) alkyl halide, (3) magnesium sulfonate, (4) hydrocarbon corresponding to the RMgX when insufficient ester is used and (5) the improvement in alkylation yield noted when an excess of ester is used.

The alkyl halides formed in accordance with Reaction 4 may also be prepared from the alkyl sulfonate when the –MgX group is attached to practically all elements, and not only to carbon as in the Grignard reagent. This was shown when *n*-butyl halides were obtained from *n*-butyl *p*-toluenesulfonate and ethoxymagnesium iodide (C_2H_5OMgI), phenoxymagnesium iodide (C_6H_5OMgI), *p*-tolylsulfinylmagnesium bromide (p-$CH_3C_6H_4S(=O)OMgBr$), methylanilinomagnesium bromide ($C_6H_5N\text{-}(CH_3)\text{-}MgBr$), thiophenylmagnesium iodide (C_6H_5SMgI), magnesium iodide and magnesium bromide.

The formation of RX from the alkyl sulfonate and the magnesium halides is of more than passing interest. Some magnesium halide is formed in the ordinary preparation of all Grignard reagents, but the extent of this side reaction is altogether too slight to account for the high yield of RX compound obtained in the several experiments with alkyl sulfonates. Of much greater significance is its bearing on the constitution of the Grignard reagents. Very recently a renewed interest has been shown in Jolibois'[8a] formula for oganomagnesium halides. He suggested that RMgX compounds are really magnesium dialkyls or diaryls with magnesium halide, and that the correct formulation is $R_2Mg + MgX_2$ instead of RMgX. For our present purposes it is of no great significance whether we ascribe

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[8] (a) Jolibois, *Compt. rend.*, **155**, 353 (1912); **183**, 971 (1926); (b) Kierzek, *Bull. soc. chim.*, **41**, 1299 (1927); (c) Grignard, *Compt. rend.*, **185**, 507 (1927); Terentiev, *Z. anorg. allgem. Chem.*, **156**, 73 (1926); Job, *Bull. soc. chim.*, **39**, 583 (1926); Ivanoff, *Compt. rend.*, **185**, 505 (1927). Meisenheimer and Schlichenmaier, *Ber.*, **61**, 720 (1928), have just reported on the molecular weight and the constitution of the Grignard reagent. In dilute solutions the organomagnesium halides are apparently monomolecular and therefore best represented as RMgX and not as $R_2Mg + MgX_2$.

to the Grignard reagents the "mixed molecule" formula or whether we designate this complex as being in equilibrium with the RMgX form.

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (10)$$

Gilman and Schulze[9] have shown that the following equilibrium under certain conditions exists between beryllium dialkyls and alkylberyllium halides.

$$2RBe \rightleftharpoons R_2Be + BeX_2 \qquad (11)$$

In this connection it is interesting to note that other inorganic halides have split alkyl sulfonates to give alkyl halides. Kenyon, Phillips and Turley,[3] for example, used lithium chloride, sodium bromide and potassium iodide with their lactyl sulfonate to get the corresponding ethyl α-halogenopropionates. Further studies[10] of the chemistry of R_2Mg compounds should throw more light on this problem.

The formation of sulfones (Reaction 2) is not restricted to aryl esters of sulfonic acids. *n*-Butyl *p*-toluenesulfonate and phenylmagnesium bromide gave, in addition to large amounts of normal products that would be expected from Reactions 1, 3 and 4, a small quantity of phenyl *p*-tolyl sulfone. A corresponding reaction was reported some years before by Ferns and Lapworth,[1] and Strecker,[1] who showed that ethyl ethanesulfonate and phenylmagnesium bromide underwent reactions in accordance with 1 and 2.

Experimental

In general, stock solutions of the appropriate Grignard reagent in ether were used. These solutions were filtered free of any unused magnesium and aliquots[11] and were slowly added to the ester until a positive color test[12] was obtained. In a few cases the ester was added to the Grignard reagent, but no essential differences were noted. After refluxing for one to two hours, the mixture was hydrolyzed by iced acid. The ether layer, after washing with water, was steam distilled in order to effect a more ready separation of alkyl halide and hydrocarbon from any unused ester. All of the alkyl halides were identified by conversion to the alkylmercuric halides,[13] and these in turn were identified by a mixed melting point determination made with authentic specimens.

[9] Gilman and Schulze, *J. Chem. Soc.*, **131**, 2663 (1927); THIS JOURNAL, **49**, 2904 (1927). In the latter reference (p. 2907) attention is directed to the possibility of the same equilibrium with RMgX compounds. The same idea has been suggested by Grignard (see ref. 8c of this paper).

[10] Gilman and Schulze, THIS JOURNAL, **49**, 2328 (1927). This paper reports a study of the reaction between magnesium diethyl and acetyl chloride.

[11] The yields of Grignard reagent were assumed to be those determined by Gilman and McCracken, *ibid.*, **45**, 2462 (1923).

[12] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925); *Bull. soc. chim.*, **41**, 1479 (1927).

[13] Marvel, Gauerke and Hill, THIS JOURNAL, **47**, 3009 (1925); also, Hill, *ibid.*, **50**, 167(1928).

The magnesium sulfonates were obtained from the water layer by crystallization after concentration. They are much less soluble in water than the magnesium halides. Some of the magnesium sulfonates were analyzed for water of crystallization as well as for magnesium in the anhydrous salt.

TABLE I

Ester	G.	Mole	–MgX compound	Hydrocarbon	G.	%	RX compound	G.	%
$(C_2H_5)_2SO_4$	16	0.1	MgI_2	......	..	..	C_2H_5I[a]	1.5	10
$(C_2H_5)_2SO_4$	38	.25	C_2H_5MgBr	......	..	..	C_2H_5Br	..	..
C_2H_5-*p*-$OSO_2C_7H_7$	20	.1	C_6H_5MgI	$C_2H_5C_6H_5$	3	45	C_2H_5I	2.5	32
n-C_4H_9-*p*-$OSO_2C_7H_7$	91.2	.4	$MgBr_2$	......	..	..	*n*-C_4H_9Br[b]	38	71
n-C_4H_9-*p*-$OSO_2C_7H_7$	91.2	.4	*n*-C_3H_7MgI	......	..	..	*n*-C_4H_9I[c]	20	67
n-C_4H_9-*p*-$OSO_2C_7H_7$	91.2	.4	$C_6H_5CH_2MgCl$	*n*-$C_5H_{11}C_6H_5$	20	67	*n*-C_4H_9Cl[d]	..	..
n-C_4H_9-*p*-$OSO_2C_7H_7$	91.2	.4	C_6H_5MgBr	*n*-$C_4H_9C_6H_5$	17	64	*n*-C_4H_9Br[e]	18	67
n-C_4H_9-*p*-$OSO_2C_7H_7$	23	.1	C_2H_5OMgI	......	..	..	*n*-C_4H_9I	12	67
n-C_4H_9-*p*-$OSO_2C_7H_7$	23	.1	C_6H_5OMgI	......	.	..	*n*-C_4H_9I[f]	10	54
n-C_4H_9-*p*-$OSO_2C_7H_7$	186	.8	C_6H_5SMgI	......	..	..	*n*-C_4H_9I[g]	43	67
n-C_4H_9-*p*-$OSO_2C_7H_7$	228	1.0	$C_6H_5N(CH_3)MgBr$	......	..	..	*n*-C_4H_9Br[h]	22	30

[a] In studies where esters other than those of the halogen acids (or RX compounds) were treated in ether with magnesium, diethyl sulfate gave a positive color test when a trace of iodine was added. Unquestionably this was due to the formation of some magnesium iodide, which split the diethyl sulfate to form ethyl iodide and this then reacted with the magnesium present to give ethylmagnesium iodide.

[b] An 85–87% yield of magnesium *p*-toluenesulfonate was obtained.

[c] The quantity of *n*-propylmagnesium bromide required for a positive test was 0.2 mole. No attempt was made to separate the low boiling *n*-heptane. The yield of magnesium *p*-toluenesulfonate was 65 g. or 70%.

[d] *n*-Butyl chloride was not isolated here; however, qualitative tests showed it to be present. The large quantity of ether used in this experiment was undoubtedly responsible for the difficulty in separating the butyl chloride. This was shown in a blank experiment where 18 g. of butyl chloride was added to the same volume (550 cc.) of ether and fractional distillation with the same column gave no separation. From a corresponding reaction, using one mole of ester and one mole of benzylmagnesium cloride, Marvel[4] succeeded in separating butyl chloride. The yield of magnesium *p*-toluenesulfonate from this experiment was 70%.

[e] In this experiment 0.22 mole of phenylmagnesium bromide was required to give a positive color test that persisted after two hours of refluxing. The yield of magnesium *p*-toluenesulfonate was 86 g. or 86.5%. The anhydrous salt was analyzed for magnesium after drying to constant weight at 110°. *Anal.* Calcd. for $(C_7H_7SO_3)_2Mg$: Mg, 6.64. Found: 6.65, 6.64. A sodium hydroxide extraction of the ether layer gave some phenol. The residue from steam distillation gave 2.0 g. of phenyl-*p*-tolyl sulfone. This was identified by a mixed melting point determination with an authentic specimen.

[f] The yield of magnesium *p*-toluenesulfonate was 67%. In another run a special search failed to reveal any *n*-butylphenyl ether. The phenol was almost quantitatively recovered as 2,4,6-tribromophenol.

[g] The *p*-thiophenylmagnesium iodide was prepared from 44 g. or 0.4 mole of *p*-thiophenol and an equivalent quantity of *n*-propylmagnesium iodide. Subsequent to hydrolysis the ether layer when extracted with sodium hydroxide yielded no thiophenol. The yield of *n*-butylphenyl sulfide was 39 g. or 52%.

[h] The methylanilinomagnesium bromide was prepared from 55 g. or 0.5 mole of methylaniline and ethylmagnesium bromide. Twenty g. of an amine boiling at 225–230° was obtained. This was very probably the expected methyl-*n*-butylaniline, $C_6H_5N(CH_3)(n\text{-}C_4H_9)$. The boiling point agrees with that reported by Komatsu, *J.*

Coll. Sci. Imperial University of Tokio, **3**, 371 (1912), *C. A.*, **7**, 1021 (1913), but not with that reported by Fröhlich and Wedekind, *Ber.*, **40**, 1648 (1907). Accordingly, the picrate was prepared and found to melt at 93° and not at 141–142°, as reported by Komatsu. There is a possibility of a typographical error in Komatsu's work, because among the large number of picrates reported by him is a related one melting at 93–94°, namely, methyl-*iso*-amylaniline.

p-Toluenesulfonic Ester of Ethyl Lactate and Phenylmagnesium Bromide.—From 12 g. or 0.04 mole of the ester and 0.05 mole of phenylmagnesium bromide, there was obtained 4 g. or a 55% yield of ethyl α-bromopropionate. Its identity was confirmed by the preparation of the ammonium salt prepared from m-nitraniline according to the method of Bischoff.[14] A mixed melting point determination was then made with an authentic specimen and the observed melting point was 247–248°.

Because of the small size of the experiment none of the expected ethyl α-phenylpropionate was isolated. Probably some of the phenyl ester, if formed, reacted with the excess of Grignard reagent to give some of the corresponding ketone or ester. These products are to be sought in a larger run, for they should be present if Reactions 3 and 4 are correct and if the lactyl ester is not an exceptional compound.

Ethyl Cyclohexylsulfonate and Phenylmagnesium Bromide.—From 35 g. or 0.18 mole of ester and a slight excess (color reaction) of phenylmagnesium bromide, there were obtained 3.5 g. of ethylbenzene, some ethyl bromide (characterized as ethylmercuribromide) and 1 g. of a compound melting at 107°. It was thought that this solid was cyclohexylphenyl sulfone. However, this could not be confirmed because when experiments were carried out to synthesize such a sulfone by standard procedures, the melting point of the synthetic compound was 73°. This latter compound was prepared by the oxidation of the sulfide obtained from sodium thiophenate and bromocyclohexane. The properties of the cyclohexylphenyl sulfide are: b. p. 145° (11 mm.); $d_{20}^{20} = 1.0031$; $n_{25} = 1.5663$. The magnesium cyclohexylsulfonate was analyzed.

Anal. Calcd. for $(C_6H_{11}SO_3)_2Mg{\cdot}6H_2O$: H_2O, 24.88. Found: 24.28, 24.25. Calcd. for $(C_6H_{11}SO_3)_2Mg$: Mg, 7.45. Found: 7.34, 7.45.

This experiment with ethyl cyclohexylsulfonate shows that alkyl alicyclic sulfonates alkylate after the manner of alkyl arylsulfonates according to Reaction 1.

n-Butyl p-Toluenesulfonate and Ethylmagnesium Bromide with Water.—By means of the color test[11] it was shown that 0.1–0.12 mole of water in ether was required to destroy 0.1 mole of ethylmagnesium bromide. To this mixture, which may be magnesium bromide and magnesium hydroxide and not basic magnesium bromide,[8b] there was added 23 g. or 0.1 mole of n-butyl p-toluenesulfonate. After refluxing for two hours and then working up in the customary manner, there were obtained 2 g. or 14% of n-butyl bromide and 18 g. or 40% of magnesium p-toluenesulfonate.

n-Butyl p-Toluenesulfonate and Bromomagnesium p-Tolylsulfinate (p-$CH_3C_6H_4S({=}O)OMgBr$).—The bromomagnesium sulfinate was prepared by the addition of sulfur dioxide to a 0.4 mole solution of p-tolylmagnesium bromide until there was no color reaction.[11] After reaction with 92.4 g. or 0.4 mole of n-butyl p-toluenesulfonate, there were obtained 32 g. or 58% of n-butyl bromide and 80 g. of a mixture of the magnesium salts of p-toluenesulfinic and p-toluenesulfonic acids. From another run, 7 g. of p-toluenesulfinic acid was obtained.

n-Butyl p-Toluenesulfonate and Iodomagnesium β-Naphthalenesulfonate, β-$C_{10}H_7SO_2OMgI$.—The anhydrous β-naphthalenesulfonic acid was prepared according to the directions of Kraft and Roos[15] and was checked by a melting point determination

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[14] Bischoff, *Ber.*, **30**, 2766 (1897).

[15] Kraft and Roos, *Ber.*, **26**, 2823 (1893).

in vacuo[16] and a neutralization equivalent. Sufficient anhydrous acid was used to react with 0.2 mole of methylmagnesium iodide until no color test was obtained. From the iodomagnesium sulfonate obtained in this manner and 46 g. or 0.2 mole of *n*-butyl *p*-toluenesulfonate, there was obtained 12 g. or 33% of *n*-butyl iodide.

A part of the magnesium β-naphthalenesulfonate, which incidentally is less soluble in water than magnesium *p*-toluenesulfonate, was analyzed after drying to constant weight at 110°.

Anal. Calcd. for $(\beta\text{-}C_{10}H_7SO_3)_2Mg$: Mg, 5.99. Found: 6.09.

Phenyl *p*-Toluenesulfonate and Magnesium Bromide.—An ether–toluene solution containing 50 g. or 0.2 mole of phenyl *p*-toluenesulfonate and 0.25 mole of magnesium bromide etherate was refluxed for two hours at 100°. After hydrolysis, an ether extract of the steam distillate gave no test for halogen and there was no indication of the formation of magnesium *p*-toluenesulfonate. This experiment illustrates a difference between aryl and alkyl sulfonates (see Reactions 1 and 2).

Summary

Alkylation is not the only reaction that takes place when alkyl sulfonates are treated with organomagnesium halides. Alkyl halides are also formed. The reactions proposed to account for these products have a direct bearing on the formula for the Grignard reagent proposed some time ago by Jolibois.

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NEW CONDENSATIONS OF KETONES WITH PHENOLS. THE PHORONE DI-META-CRESYL ETHER

BY JOSEPH B. NIEDERL

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Introduction

The importance of the condensations occurring between aldehydes and phenols gave the impulse to a number of investigations of the behavior of ketones toward phenols under the influence of dehydrating agents.

Previously the following four types of condensations of ketones with phenols had been established: (1) the formation of diphenylmethane derivatives,[1,2] (2) the formation of ketals,[2,3,4] (3) the formation of molecular addition compounds and (4) the formation of oxygen heterocyclics.[5]

It has now been found that diaryl derivatives of di-*iso*-butyl ketone

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[16] Witt, *Ber.*, **48**, 743 (1915).

[1] Dianin, *J. Russ. Phys.-Chem. Soc.*, **1**, 488–517 (1891).

[2] Mackenzie, *J. Chem. Soc.*, **121**, 1695 (1922).

[3] Claisen, *Ber.*, **29**, 1005 (1896); *Ber.*, **31**, 1010 (1898).

[4] Clough, *J. Chem. Soc.*, **89**, 771 (1906); *ibid.*, **26**, 170 (1910); Schmidlin and Lang, *Ber.*, **43**, 2806 (1910).

[5] Chem. Fabriken vorm. Weiler ter Mer, Ger. pat., 357,755.