Anal. Subs., 0.2872: AgBr, 0.1886. Calcd. for $C_{11}H_9O_4Br$: Br, 28.04. Found: 27.95.

1,6-Bromonaphthol.—This compound dissolved readily in hot water from which it separated slowly in the form of long, fibrous needles; m. p., 129–130°; yield, 0.3 g. from 4 g. of the paraconic acid, or about 10%.

Anal. Subs., 0.1384: AgBr, 0.1162. Calcd. for $C_{10}H_7OBr$: Br, 35.85. Found: 35.73.

1,7-Bromonaphthol.—This naphthol crystallized from hot water in cotton-like masses which slowly turned dark when exposed to light. It resembled the 1,6-isomer very closely, having a marked phenolic odor and giving a deep purple color when treated with ferric chloride solution; m. p., 105.5–106.5°.

Anal. Subs., 0.1665, 0.2040: AgBr, 0.1417, 0.1735. Calcd. for $C_{10}H_7OBr$: Br, 35.85. Found: 36.20, 36.19.

Summary

1. *M*- and *p*-bromophenylparaconic acids have been prepared and from them by the Erdmann ring closure the 1,6 and 1,7 bromonaphthols, respectively.

2. The five known monobromo derivatives of α-naphthol have been listed and their usefulness as reference substances in orientation work has been pointed out.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PREPARATION OF HYDROCARBONS BY THE REACTION BETWEEN ALKYL SULFONATES AND ORGANOMAGNESIUM HALIDES

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Introduction

Many methods are available in organic synthesis for the preparation of hydrocarbons. However, syntheses involving the preparation of unsymmetrical hydrocarbons are generally somewhat indirect.[1] A number of these indirect methods have a circumscribed utility for several reasons: they often involve the use of expensive materials, some of the reactions used may be unreliable in the determination of structure and the yields are frequently rather low.

The Grignard reagent (RMgX) has long been used in a wide variety of direct and indirect[2] syntheses for the preparation of hydrocarbons. Recently, Gilman and Hoyle[3] reported on the preparation of hydrocarbons

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[1] Maihle has reviewed recently methods for the preparation of hydrocarbons; *J. usines gaz.*, **48**, 34 (1924); *C. A.*, **18**, 1464 (1924).

[2] In particular, Clarke and co-workers, *Am. Chem. J.*, **39**, 572 (1908), etc., who prepared a number of isomeric paraffin hydrocarbons by indirect methods.

[3] Gilman and Hoyle, THIS JOURNAL, **44**, 2621, 2969 (1922).

and other classes of compounds by the direct introduction of an ethyl group by the reaction between organomagnesium halides and diethyl sulfate. Prior to that time, Werner and Zilkens[4] and Houben[5] used dimethyl sulfate in an analogous manner for the introduction of a methyl group. The list of dialkyl sulfates has been extended recently by Bert who used di-*iso*propyl sulfate,[6] and mixed dialkyl sulfates[7] where one of the groups is ethyl.

Although satisfactory yields of pure materials can be obtained by most of these methods, they are necessarily restricted by the decidely small number of readily available dialkyl sulfates. Bert's reaction with mixed dialkyl sulfates is unfortunately of little use, for apparently only one alkyl group can be introduced and this is always the one of lower weight. In some other reactions with mixed dialkyl sulfates it is possible to introduce both groups.[8]

It has been found possible to introduce a rather wide and fairly comprehensive series of alkyl groups by treating the Grignard reagent with alkyl esters of aromatic sulfonic acids. Ferns and Lapworth[9] found that ethylbenzene was the main product of the reaction between ethyl *p*-toluenesulfonate and phenylmagnesium bromide. Wedekind and Schenck[10] in a reaction between ethylmagnesium bromide and ethyl *p*-toluenesulfonate obtained magnesium *p*-toluenesulfonate and apparently no butane. It is stated that this reaction was completed before the work of Ferns and Lapworth. Subsequently, a preliminary study by Gilman and Beaber[11] showed that halogen-alkyl groups can be introduced by the reaction between halogen-alkyl esters of aromatic sulfonic acids and organomagnesium halides.

The reaction between alkyl sulfonates and the Grignard reagent may be formulated as follows: $2\ p\text{-}CH_3C_6H_4SO_2O\text{-Alkyl} + 2RMgX = 2R\text{-}Alkyl + (p\text{-}CH_3C_6H_4SO_3)_2Mg + MgX_2$. It takes place quite smoothly at the boiling point of ether and gives yields which correspond with those given by dialkyl sulfates.

There is one limitation to the general applicability of this synthesis. When the Grignard reagent has an R group of low weight, as in propylmagnesium and butylmagnesium bromides, the yield of aliphatic hydro-

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[4] Werner and Zilkens, *Ber.*, **36**, 2116 (1903).

[5] Houben, *ibid.*, **36**, 3083 (1903); **37**, 488 (1904). Also, Werner, *ibid.*, **36**, 3618 (1903).

[6] Bert, *Compt. rend.*, **176**, 840 (1923).

[7] Bert, *ibid.*, **178**, 1182 (1924).

[8] Thayer, THIS JOURNAL, **46**, 1044 (1924).

[9] Ferns and Lapworth, *Proc. Chem. Soc.*, **28**, 18 (1912); *J. Chem. Soc.*, **101**, 273 (1912).

[10] Wedekind and Schenck, *Ber.*, **54**, 1604 (1921).

[11] Gilman and Beaber, THIS JOURNAL, **45**, 839 (1923).

carbon is so low as to make the reaction of no value. Fortunately, however, this is only an apparent objection for two reasons. First, the simpler paraffins having 6, 7 and 8 carbon atoms can be prepared conveniently by other methods.[2] Second, it is possible to prepare aliphatic hydrocarbons having about ten carbon atoms by transposing, so to speak, the alkyl groups in the Grignard reagent and the ester. For example, tetradecane ($C_{14}H_{30}$) can be prepared from laurylmagnesium bromide ($C_{12}H_{23}MgBr$) and ethyl *p*-toluenesulfonate ($CH_3C_6H_4SO_2OC_2H_5$), even though ethylmagnesium bromide would probably give practically none of this hydrocarbon when treated with lauryl *p*-toluenesulfonate.

Obviously, the same compound could be obtained by using intermediate radicals, such as heptylmagnesium bromide and heptyl *p*-toluenesulfonate. However, the best yields of aliphatic compounds are obtained with the largest alkyl group in the Grignard reagent. Arylmagnesium halides, such as phenylmagnesium bromide, appparently give good yields with all alkyl esters. Also, an aryl-alkyl Grignard reagent, such as benzylmagnesium chloride, reacts with all esters to give appreciably higher yields than those obtained with arylmagnesium halides.

The same low yields, when the alkyl group in the RMgX compound is small, were obtained in a related study by Gilman and Beaber.[11] They reported a significantly low yield in the reaction between butylmagnesium bromide and halogen-alkyl sulfonates. These several observations raised an element of doubt concerning the relatively high yield of *n*-hexane obtained by Gilman and Hoyle[3] in the reaction between butylmagnesium bromide and diethyl sulfate. Several carefully repeated experiments showed the yield to be virtually insignificant and emphasized the necessity of slow fractional distillation.

A later paper will report a study of the reaction between aryl sulfonates and the Grignard reagent. An aryl group cannot be introduced by this reaction; instead, sulfones and the corresponding phenols are obtained.

Preparation of the Esters

Ferns and Lapworth,[9] in a study on the preparation and properties of sulfonic esters, have made a critical review of standard methods for the preparation of these compounds. Subsequently, Földi,[12] Hahn and Walter,[13] and Clemo and Perkin[14] by various alterations and innovations improved the yields of earlier known esters and extended the synthesis to include new types.

The method of Földi[12] involves a Schotten-Baumann reaction between the alcohol, benzenesulfonyl chloride and 20–30% sodium hydroxide.

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[12] Földi, *Ber.*, **53,** 1836 (1920).

[13] Hahn and Walter, *ibid.*, **54B,** 1531 (1921).

[14] Clemo and Perkin, *J. Chem. Soc.*, **121,** 642 (1922). See also Ref. 11.

This was used by us for the preparation of allyl *p*-toluenesulfonate. However, it was found possible to prepare *n*-propyl-*p*-toluenesulfonate by the method of Hahn and Walter[13] in a yield which was 15% in excess of that reported by Földi; the method of Hahn and Walter was used accordingly in the preparation of all other alkyl esters of *p*-toluenesulfonic acid.

It is possible that the method of Földi may be preferred for certain esters. However, the ease with which alkyl esters of sulfonic acids undergo hydrolysis would indicate that Hahn and Walter's method, using solid potassium hydroxide, dry ether and a low temperature, gives an assurance of somewhat higher yields. The following new esters of *p*-toluenesulfonic acid have been prepared by the use of this method: *n*-butyl, *iso*butyl, *sec*-butyl, *n*-amyl and benzyl.

Several unsuccessful attempts were made to prepare the corresponding esters of two tertiary alcohols: namely, *tert*-butyl alcohol and triphenylcarbinol. Ferns and Lapworth[9] tried to prepare the benzyl ester. In an experiment by them where *p*-toluenesulfonyl chloride was treated in ether with alcohol-free potassium benzyloxide, the desired benzyl ester may have been an intermediate product in the formation of dibenzyl ether. When they mixed *p*-toluenesulfonyl chloride, pyridine and benzyl alcohol, a rapid rise in temperature was noted, but in every case the products were soluble in water.

Clemo and Perkin[14] obtained good yields of chloro-ethyl esters by heating the sulfonyl chloride with an excess of ethylene chlorohydrin. Although the authors[11] found this method to be quite satisfactory for the preparation of other halogen-alkyl esters, they had little success with it in a few experiments where *iso*propyl and *n*-butyl alcohols were used. In these runs either the product was water-soluble or much unaltered acid chloride was recovered. An equal lack of success was noted when the reaction mixture was allowed to stand at room temperature for some time. When a small amount of water-insoluble oil was obtained it could not be distilled under reduced pressure without charring, even after thoroughly washing with dil. alkali and then drying the ether extract with calcium chloride or potassium carbonate.

Using the method of Hahn and Walter, powdered potassium hydroxide was slowly added to a well-stirred ether solution containing equivalent weights of freshly distilled *p*-toluenesulfonyl chloride and the alcohol. The temperature was not allowed to rise above 4° and this necessitated, at first, small additions of potassium hydroxide (not more than 0.5 g. at a time) because of the vigor of the reaction. The quantity of alkali required, so that a filtered portion gave no test for halogen, varied between small limits, but was generally about two equivalents. After the reaction mixture had been poured into iced water, it was extracted with ether. The ether layer after separation was washed with water and then dried with potassium carbonate. Ether and the occasional small amounts of unchanged alcohol were removed by vacuum distillation.

The use of ether is preferred to that of benzene because of the avoidance of troublesome emulsions. Apparently potassium carbonate is a better drying agent than calcium chloride. Often, after drying with calcium chloride, a fine white precipitate was formed during vacuum distillation of the ester and decomposition then set in generally. It is probable that the potassium carbonate helps by removing sulfonic acid formed by the hydrolysis of these somewhat sensitive esters. Certainly the ever-present danger of charring and deep-seated decomposition during distillation is reduced by this drying agent. For example, it was found possible to distil propyl *p*-toluenesulfonate at 154–156° (3 mm.), whereas Hahn and Walter report that the ester decomposes when heated above 150° in a vacuum.[15]

Reaction of Esters with the Grignard Reagent

The reaction between an ester and the Grignard reagent was carried out in a manner essentially like that described in related studies.[3,11] An equivalent amount of ester dissolved in an equal volume of ether was slowly added to the RMgX compound. A fairly vigorous reaction took place on the first addition of ester. The thick mixture was refluxed and stirred for two or three hours and then poured onto crushed ice to which was later added dil. hydrochloric or sulfuric acid.

After the ether extract was washed with water, it was dried by standing for several hours over potassium carbonate. The solution was then

TABLE I

PREPARATION OF ESTERS

These esters are obtained from equivalent quantities of *p*-toluenesulfonyl chloride and an alcohol.

Alcohol	G.	Moles	Yield of corresponding ester G.	%	Boiling point °C.	Mm.	d_4^{20}	n_D^{20}	% S Calcd.	Found
n-Propyl	15	0.25	45.5	85	154–156	3	1.144	1.4998	...	...
n-Butyl[a]	74	1.0	126	50.9	163–165	3	1.120	1.5050	14.04	14.45 14.03
iso-Butyl	74	1.0	148	64.9	163–165	3	1.125	1.5050	14.04	13.8
sec-Butyl	37	0.5	37.5	32.9	decomp.[b]		1.140	1.5100	14.04	13.8
n-Amyl	44	.5	90	74.4	169–170	3	1.100	1.5028	13.22	13.26
Benzyl[c]	54	.5	105	80	m. p. = 55°		...	....	...	...
Allyl[d]	58	1.0	165	77.8	148–150	3	1.175	1.5242	15.09	15.82 15.86

[a] The *n*-butyl *p*-toluenesulfonate was prepared by the Eastman Kodak Co., Rochester, N. Y., before we made the compound, and their compound has been used in most of the preparations. They prepared this ester and the *n*-propyl ester by refluxing the acid

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[15] The esters show a decided tendency at times to be superheated. Propyl *p*-toluenesulfonate was heated to 165–168° (3 mm.) without any evidences of decomposition.

chloride with a 10% excess of the corresponding alcohols. Their yields by this method were 26.1% and 31.5%, respectively. However, their methyl *p*-toluenesulfonate was prepared essentially according to the method of Földi[12] in 75% yield.

[b] An attempted distillation at 2mm. pressure resulted in complete decomposition before the pale yellow liquid showed any evidence of boiling. The analysis indicates that the compound can be obtained in a fair state of purity by careful washing and drying.

[c] The reaction mixture of benzyl alcohol and *p*-toluenesulfonyl chloride when poured into iced acid gave a solid that was only sparingly soluble in ether. After dissolving in a mixture of ether and benzene it was dried by potassium carbonate. When the solution was concentrated under a vacuum a voluminous white precipitate was formed. This was filtered by suction and the crystals were found to melt sharply at 55°. However, when the crystals were allowed to stand in a highly evacuated desiccator for about one hour, they changed to a dark tarry mass which was almost completely soluble in water. In a duplicate run, after the ether was distilled at 15 mm., a thick, pale yellow oil was formed. This solidified on cooling. No analysis was made. The reaction with benzylmagnesium chloride, however, shows it to be the desired ester. Benzyl benzenesulfonate decomposes only slowly over several days.[13]

[d] In a first run, an attempt was made to distil the ester after it had stood for several months. Charring set in after a small amount of *p*-toluenesulfonic acid distilled. In some distillations of a duplicate run, decomposition took place with almost explosive violence. Using rather elaborate precautions to prevent superheating it was found possible to distil a 20g. sample. The sulfur analyses of this distillate agreed with the high values obtained from the oil which was not distilled: namely, 15.84% and 15.86%.

TABLE II

REACTION OF ESTERS WITH GRIGNARD REAGENTS

The hydrocarbons described are those obtained from equivalent[a] quantities of RMgX compound and the ester of *p*-toluenesulfonic acid.

RX compound	Ester	Moles	Compound formed	G.	Yield %	Boiling[a] point °C.	d_4^{20}
Bromobenzene	Methyl	0.3	Toluene	10.5	38	109–112	...
Benzyl chloride[b]	Methyl	.3	Ethyl-benzene	13	40.9	134–137	...
p-Bromotoluene	Methyl	.3	*p*-Xylene	9.3	29.2	135–139	0.862
Bromobenzene	Ethyl	1.0	Ethyl-benzene[c]	31.5	29.7	135–137	.874
Benzyl chloride	Ethyl	.5	*n*-Propyl-benzene	23	38.3	154–159	.860
p-Bromotoluene	Ethyl	.5	*p*-Ethyl-toluene	22	36.6	156–160	.862
α-Bromonaphthalene	Ethyl	.2	α-Ethyl-naphthalene[d]	6	19.2	246–250	1.019
γ-Chloropropyl benzene	Ethyl	.2	*n*-Amyl-benzene	11.5	39.5	198–202	0.858
Bromocyclohexane	Ethyl	.2	Ethyl-cyclohexane	2	8.9	128–132	...
Lauryl bromide	Ethyl	.15	*n*-Tetradecane[e]	8	27	238–240	0.761
Benzyl chloride	*n*-Propyl	.21	*n*-Butyl-benzene	10	35.6	178–183	.862
Benzyl chloride	*n*-Butyl	.3	*n*-Amyl-benzene	11	24.6	198–202	.864
n-Heptyl bromide	*n*-Butyl	.14	*n*-Undecane[f]	2.2	14.1	193–196	...
Benzyl chloride	*iso*-Butyl	.2	*iso*-Amyl-benzene	9.8	33.1	189-191	0.856
Benzyl chloride	*sec*-Butyl	.2	1-Phenyl-2-methyl-butane[g]	8	29.9	188–191	.861
Benzyl chloride	*n*-Amyl	.1	*n*-Hexyl-benzene	7.3	45.1	214–216	.862
Benzyl chloride	Allyl	.4	1-Phenyl-3,4-butylene	25	47	175–177	.906
Benzyl chloride	Benzyl	.4	Dibenzyl[h]	40	55	.....	...

[a] The temperatures recorded in this paper are uncorrected.

[b] After removing the ethyl benzene by distillation there was recovered from the residue about 3 g. of a hydrocarbon which, after several recrystallizations from alcohol, melted at 119–120°. The same compound was obtained in various quantities from practically all of the reactions of benzylmagnesium chloride and alkyl esters of *p*-toluenesulfonic acid. The compound has not yet been identified.

[c] The residue from the vacuum distillation gave 9 g. of diphenyl. A large part of

this is due probably to a reaction like the Wurtz-Fittig which takes place during the preparation of RMgX compounds. Corresponding symmetrical hydrocarbons were obtained in other runs.

[d] In a first experiment considerable quantities of naphthalene were recovered. Because this indicates much unchanged organomagnesium halide, the reaction mixture in a second run was refluxed for 10 hours. Even in this run which yielded 6 g. of α-ethyl naphthalene, 8 g. of naphthalene was obtained. In this preparation and in those which follow in Table II a small excess of ester was used.

[e] In addition, 3 g. of *n*-dodecane distilling at 214–217° was obtained.

[f] In addition, 5 g. of *n*-heptane distilling at 95–98° was obtained. Earlier runs between *n*-heptylmagnesium bromide and ethyl *p*-toluenesulfonate gave a fraction which very likely contained *n*-nonane. Separation from heptane, probably formed from unreacted RMgX compound, was difficult because of the small quantities used.

[g] This compound was previously prepared by Dumesnil, *Ann. chim.*, [9] **8,** 70 (1917). The boiling point determined by him is 102° (15 mm.). At 12 mm. we found that it was 95–97°; n_{D}^{20}, 1.4724.

[h] A vigorous reaction which necessitated cooling took place on the addition of the benzyl ester to benzylmagnesium chloride. The 40 g. of dibenzyl was obtained by vacuum distillation. The solid obtained melted at 51.5°. Inasmuch as the benzylmagnesium chloride was prepared according to the method that gives a 94% yield of this RMgX compound it is evident that only a small amount of the dibenzyl could be due to a Wurtz-Fittig reaction. See Gilman and McCracken, THIS JOURNAL, **45,** 2462 (1923).

filtered directly into a small Claisen flask heated on a water-bath to remove the ether by distillation. It was found desirable to distill the resulting oil in a vacuum at first in order to remove any unchanged ester, which generally undergoes decomposition when heated at too high a temperature. Subsequently, that fraction containing the desired hydrocarbon was fractionated and re-fractionated by distillation under atmospheric pressure.

Discussion of Results

The yields obtained by treating an RMgX compound with methyl or ethyl *p*-toluenesulfonate exceed in some cases those obtained with dimethyl or diethyl sulfate.[3,4,5] However, in most preparations the latter are to be preferred because of the significant advantage in cost when one considers the alkylating content of the respective esters. It is possible that the same may be true with other sulfates such as dipropyl, dibutyl, etc. However, even granting that most of the important dialkyl sulfates can be made available at a reasonable cost, the alkyl esters of aromatic sulfonic acids may still enjoy the advantage of superior yields. This is made somewhat evident by the rather low yields, 10%, obtained by the use of di-*iso*-propyl sulfate.[6] The *iso*- and *sec*-butyl *p*-toluenesulfonates used in this study have given yields around 30%.

There appears to be only a small correlation between the yield obtained from a given RMgX compound and an homologous series of esters. Using benzylmagnesium chloride, it is noted that the yield drops regularly from the methyl to ethyl to *n*-propyl and to the *n*-butyl ester. However, *iso-* and *sec*-butyl esters give a higher yield than the *n*-butyl ester; the *n*-amyl gives a higher yield than any of the previously mentioned esters; the yield from the allyl ester exceeds that from the amyl ester; and, the yield from the benzyl ester exceeds that of any other ester.

Conclusion

The value of the syntheses described here and those reported earlier depends rather largely on the yield of pure compound formed. The esters can either be prepared readily and in satisfactory yields from the low priced *p*-toluenesulfonyl chloride, or most of them can be purchased.[16] It is known[17] that the Grignard reagents generally, and particularly those which appear to react best with the esters, are prepared easily and in good yields. The yield of hydrocarbon (or derivatives where substituents are not reacted on by RMgX compounds) varies somewhat, but may be said to compare favorably with most standard, essentially direct and so-called reliable methods for the introduction of an alkyl group. Obviously, the same method may be used for the attachment of alkyl groups to other elements than carbon.[3,11]

A serious criticism is to be found in the purity of product. In most preparations the product was redistilled and in a few cases a third and a fourth distillation were made. However, in any specific preparation this difficulty can be reduced somewhat. It is possible by a proper choice of ester and Grignard reagent to diminish the extent of interfering impurities.

Such impurities may come in part from the ester and from the RMgX compound. The ester may contribute one of its products of hydrolysis, the alcohol. The Grignard reagent will give the symmetrical compound formed by a Wurtz-Fittig reaction, such as diphenyl in the preparation of phenylmagnesium bromide; also, the product of hydrolysis of unchanged compound, such as naphthalene from naphthylmagnesium bromide and, to a smaller extent, some unaltered RX compound and some ROH compound formed by the air oxidation of the Grignard reagent.

Experiments have shown that the slight contamination with RX and ROH compounds can be rather largely removed by heating an ether or benzene solution of the compound after the first vacuum distillation (which serves to remove any unaltered ester) with sodium, then filtering and finally redistilling.

Summary

It is shown that hydrocarbons can be prepared in fair yields when the Grignard reagent is treated with an alkyl ester of *p*-toluenesulfonic acid.

AMES, IOWA

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[16] Table I, Footnote *a*.

[17] Gilman and McCracken, THIS JOURNAL, **45**, 2462 (1923).