hydrobromide as a catalyst as in the preparation of 2,3-dimethylbutadiene-1,3. The oil layer was found to boil at 72–128°. The formation of some of a methylpentenol was indicated by the fact that the weight of the water layer was low as well as by the boiling range of the product. An attempt to complete the dehydration with oxalic acid resulted in the formation of dark, high-boiling products. About 15 g. of olefin boiling at 74–76° was collected as a mixture of two possible methylpentadienes.

Summary

A mixture of the ozonides of two octylenes has been found to catalyze the polymerization of styrene, indene, 2,3-dimethylbutadiene-1,3, a methylpentadiene, and furfuryl alcohol. It has been found to be inactive as a polymerization catalyst toward stilbene, o-hydroxybenzyl alcohol, trimethylethylene, and the mixture of octylenes from which it is made. The catalyst was active at room temperature and 100° and in a solution in toluene. The ozonide underwent a change on standing especially during the first two days after its preparation and lost a large part of its catalytic power.

MADISON, WISCONSIN

CHARACTERIZATION OF ALKYL HALIDES AND ORGANOMAGNESIUM HALIDES[1]

BY A. M. SCHWARTZ AND JOHN R. JOHNSON

Since organomagnesium halides react smoothly with aryl isocyanates to produce substituted amides that are usually crystalline solids, this reaction is suitable for the identification of organomagnesium halides and of halides that can be converted into these. Gilman and his collaborators[2] have used phenyl and α-naphthyl isocyanates for this purpose and have pointed out that α-naphthyl isocyanate enjoys some advantages over phenyl isocyanate. The most important of these appears to be the fact that the resulting α-naphthyl amides can be purified more readily than the anilides. This disadvantage attending the use of phenyl isocyanate can be minimized by avoiding an excess of the isocyanate and is more than counterbalanced, in our experience, by the fact that only a small number of the α-naphthyl amides are described in the literature. Of the ten α-naphthyl amides prepared by Gilman and Furry, five had not previously been reported. On the other hand, the anilides of all of these

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[1] A paper presented at the St. Louis Meeting of the American Chemical Society, April 18, 1928. The present report contains additional data not included in the preliminary paper.

[2] Gilman and Furry, THIS JOURNAL, 50, 1214 (1928). This article gives an excellent review of previous work dealing with the action of aryl isocyanates on organometallic halides.

acids have been described in the literature. For purposes of identification, with a minimum preparation of new compounds, it appears preferable to use phenyl isocyanate.
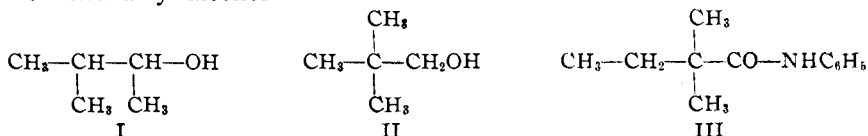
In the present study the alcohols were used as the principal starting materials, since the method lends itself to the characterization of certain secondary and tertiary alcohols and alkyl halides that cannot be identified by the usual methods. All of the isomeric propyl, butyl and amyl alcohols were carried through the series of reactions indicated below

$$R—OH \xrightarrow[PX_3]{HX} R—X \xrightarrow[ether]{Mg} R—MgX \xrightarrow[H_2O]{C_6H_5NCO} R—CO—NH—C_6H_5$$
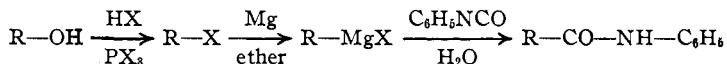
In addition to this complete series of alcohols, several other alcohols and alkyl halides were examined. The details of these preparations are shown in Table I. In practice, this method is limited principally by the yield in the conversion of the halide into the organomagnesium halide.

In general, the anilides proved to be satisfactory derivatives for identification, but in several instances the melting points of isomeric compounds differ by only a few degrees. In these cases it is necessary to prepare authentic specimens of known anilides and to use mixed melting point determinations to establish the identity of the unknown anilide. Tests of the mixed melting point procedure showed that unlike anilides of approximately the same melting point gave a marked depression of the melting point when mixed together.

Two of the isomeric amyl alcohols, 3-methylbutanol-2 (I) and 2,2-dimethylpropanol-1 (II) suffered an intramolecular rearrangement in the course of the above series of reactions. Both of these alcohols gave the anilide of dimethylethylacetic acid (III), identical with that obtained from tert.-amyl alcohol

$$CH_3—CH—CH—OH \qquad CH_3—\overset{\overset{\displaystyle CH_3}{|}}{C}—CH_2OH \qquad CH_3—CH_2—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}—CO—NHC_6H_5$$
$$\underset{\underset{\displaystyle CH_3}{|}}{}\underset{\underset{\displaystyle CH_3}{|}}{}$$

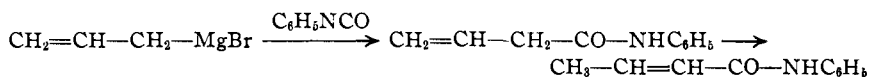$$\text{I} \qquad\qquad\qquad \text{II} \qquad\qquad\qquad \text{III}$$

It is probable that this rearrangement occurred in the conversion of the alcohols into the corresponding chlorides since the chlorides agree in physical properties with tert.-amyl chloride. Although several special methods were used in the preparation of the chlorides, such as the action of thionyl chloride in the presence of pyridine,[3] we did not obtain any anilide other than that of dimethylethylacetic acid.

In the case of allylmagnesium bromide[4] the resulting anilide was an

[3] Darzens, *Compt. rend.*, **152**, 1314 (1911); Kirner, This Journal, **50**, 1958 (1928).

[4] Gilman and McGlumphy, *Bull. soc. chim.*, [4] **43**, 1322 (1928).

oil that could not be crystallized or distilled. On warming with very dilute sulfuric acid the oil was converted to a solid, from which crotonic anilide was isolated by repeated crystallizations. In this case the original anilide was probably impure vinylacetic anilide, and the subsequent treatment effected a rearrangement to form the more stable compound in which the double bond is conjugated with the carbonyl group

$$CH_2{=}CH{-}CH_2{-}MgBr \xrightarrow{C_6H_5NCO} CH_2{=}CH{-}CH_2{-}CO{-}NHC_6H_5 \longrightarrow$$
$$CH_3{-}CH{=}CH{-}CO{-}NHC_6H_5$$

It seemed of interest to investigate the behavior of an optically active alkyl halide, in which the halogen is directly attached to the asymmetric

TABLE I

EXPERIMENTAL DATA

Alcohol	Halide of RX	Yield[a] of RMgX, %	Anilide of acid	M. p., °C. (corr.)
n-Propyl	Br	84	n-Butyric	92
Isopropyl	Br	82	Isobutyric	103
n-Butyl	Br	78	n-Valeric	63
Isobutyl	Br	81	Isovaleric	109.5
Sec.-butyl	Br	63	Methylethylacetic	108
Tert.-butyl	Cl	47	Trimethylacetic	128
n-Amyl	Br	76	n-Caproic	96
Isoamyl	Br	86	Isocaproic	108.5
Pentanol-2	Br	79	Methyl-n-propylacetic[b]	88
Pentanol-3	Br	88	Diethylacetic[c]	123–124
2-Methylbutanol-1	Br	66	Sec.-butylacetic	88
3-Methylbutanol-2	Cl	17	Dimethylethylacetic[d]	92
2,2-Dimethylpropanol	Cl	15	Dimethylethylacetic[d]	92
Tert.-amyl	Cl	38	Dimethylethylacetic	92
n-Hexyl	Br	85	n-Heptoic	69
n-Heptyl	Br	86	n-Octoic	57
dl-Octanol-2	Br	63	dl-2-Methyloctoic	72–73
d-Octanol-2	Br	61	dl-2-Methyloctoic	72–73
Cyclohexanol	Br	78	Hexahydrobenzoic	146
Benzyl	Cl	92	Phenylacetic[b]	117
Allyl	Br	62	Crotonic[c,d]	113–114

[a] The yields of RMgX are significant because the application of this method of identification is limited in practice by the successful transformation of the halide into RMgX. The yields tabulated here are merely those of typical preparations under ordinary conditions and are not usually the highest that have been attained. Data on the yields of RMgX from a variety of halides, using a standardized procedure, are found in papers by Gilman and his collaborators [THIS JOURNAL, 45, 2462 (1923); 51, 1576 (1929)].

[b] For comparison and checking, this anilide was also prepared from a pure specimen of the corresponding acid obtained by an independent synthesis.

[c] The purification of this anilide was difficult and involved an unusually great loss of material.

[d] The structure of this anilide does not correspond to that of the original alcohol; an intramolecular rearrangement occurred in this series of reactions.

carbon atom. For this purpose d-2-bromooctane was chosen, and the resulting anilide was compared with that obtained from dl-2-bromo-octane. The optically active halide was found to give a completely inactive anilide, dl-2-methyloctanoic anilide, identical in all respects with that obtained from the racemic halide.[5]

Experimental

Alcohols.—n-Propyl, isopropyl and n-butyl alcohols were obtained by fractional distillation of commercial products of high purity. With these exceptions all of the alcohols were prepared synthetically by the conventional methods (usually by Grignard syntheses) and were carefully purified. In a number of supplemental experiments we used specimens of various isomeric amyl alcohols furnished by the Sharples Solvents Corporation, who kindly supplied us with generous samples of these materials.

Alkyl Halides.—The primary and secondary alcohols were usually converted to the bromides, since the primary and secondary alkyl bromides react with magnesium more readily than the chlorides and give higher yields than the iodides. In supplementary trials on a small scale, several chlorides and iodides were used. The tertiary alcohols (and a few of the more reactive primary and secondary alcohols) were converted to the chlorides.

The straight-chain primary bromides were prepared by refluxing the alcohols with a solution of hydrobromic and sulfuric acids obtained by passing sulfur dioxide into a mixture of bromine and ice,[6] without any additional sulfuric acid. The branched chain and secondary bromides were prepared by refluxing the alcohols with 48% aqueous hydrobromic acid without the addition of sulfuric acid. Addition of the latter may lead to the production of isomeric bromides in some cases, and it is extremely difficult to separate these by fractional distillation. The tertiary alcohols were converted to the chlorides by shaking with concd. hydrochloric acid.[7] Octanol-2 and cyclohexanol were converted to the bromides by the use of phosphorus tribromide.

Organomagnesium Halides.—The Grignard reagents were prepared according to the conventional methods; a sufficient quantity of ether was used so that the resulting solutions contained from 0.5 to 1.0 mole of RMgX per liter. After standing for at least twelve hours, the solutions were decanted through a plug of glass wool and titrated with standard acid to determine the yields.[8]

Reaction with Phenyl Isocyanate.—A solution of slightly less than the theoretical amount (usually 0.90 mole) of phenyl isocyanate, dissolved in ten volumes of ether, was added dropwise to a solution of the organomagnesium halide, with shaking. It is important to avoid any hydrolysis of the isocyanate and to insure a complete reaction, in order to obtain a pure anilide. The reaction mixture was allowed to stand with occasional shaking for an hour (except for very small runs, which could be hydrolyzed after a few minutes). Hydrolysis was effected by adding, cautiously, cold water containing a little hydrochloric acid. It is necessary to shake the resulting mixture thoroughly in order to obtain a complete hydrolysis of the magnesium derivative of the anilide. The

[5] We have not yet determined whether the racemization occurs in the formation of the Grignard reagent or in the reaction of the latter with phenyl isocyanate. From theoretical considerations it appears more likely that racemization occurs in the formation of the Grignard reagent from the secondary alkyl halide.

[6] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1921**, Vol. I, p. 5.

[7] Ibid., Vol. VIII, **1928**, p. 50.

[8] Gilman, Wilkinson, Fishel and Myers, THIS JOURNAL, **45**, 150 (1923).

ether layer was separated[9] and dried with magnesium sulfate; the crude anilide remained after distilling off the solvent. The anilides were usually crystallized from ethyl ether, petroleum ether, or methyl alcohol. It is most satisfactory to effect purification by crystallization from two different solvents; the best results were obtained by a crystallization from petroleum ether followed by ethyl ether. Methyl alcohol can be used for anilides that do not respond to purification by these solvents. The resulting anilides are white crystalline solids with sharp melting points. In a few cases it was necessary to use decolorizing charcoal to obtain colorless products. The yields of the crude anilides were usually from 80–90% of the theoretical quantity, based upon the phenyl isocyanate. The losses in subsequent purification varied from 10-50%.

Procedure for Identification of Alkyl Halides.—In a dry test-tube, provided with a *cork* bearing a calcium chloride tube, is placed 0.4 g. (17 milliatoms) of magnesium turnings. A small crystal of iodine is added and the tube is heated gently until the iodine has reacted completely. The tube is allowed to cool and a solution of 1–2 g. (approximately 10 millimoles) of the dry alkyl halide in 4–5 cc. of dry ether is added. With many halides the reaction starts vigorously and it is necessary to cool the tube in a bath of cold water. In these cases it is preferable to add slowly the solution of the alkyl halide to the magnesium. If the reaction does not start spontaneously, the tube is heated gently by immersion in a beaker of warm water. After the reaction has started[10] the ether is maintained in gentle ebullition until the alkyl halide has reacted completely. After cooling, about 10 cc. of dry ether is added and the unreacted magnesium is allowed to settle. The solution is decanted quickly into another dry test-tube of large capacity, and 4–5 cc. of a 10% ethereal solution of phenyl isocyanate (3–4 millimoles) is added dropwise, with shaking. The tube is protected from atmospheric moisture and allowed to stand for a few minutes with intermittent shaking. The reaction mixture is poured *cautiously* into 20 cc. of ice water containing 1 cc. of concd. hydrochloric acid, and the mixture is agitated thoroughly. The ether layer is separated,[9] dried over anhydrous magnesium sulfate and evaporated. The residual crude anilide is crystallized from appropriate solvents, and if necessary decolorized by the addition of a little decolorizing carbon.

Summary

1. The conversion of a series of alcohols into the corresponding alkyl halides and organomagnesium halides has been investigated.

2. It has been found satisfactory to characterize these organomagnesium halides by reaction with phenyl isocyanate. The resulting anilides are crystalline solids that are suitable for identification purposes.

3. The application of this method to certain branched chain alcohols is limited by the fact that intramolecular rearrangements may lead to anilides that do not correspond in structure to the original alcohol.

4. An optically active halide, d-2-bromooctane (in which the halogen

[9] With anilides that are very slightly soluble in ether, a portion of the product separates as a crystalline precipitate and remains suspended at the interface. This portion was removed by filtration, dried and combined with the fraction obtained from the ether layer.

[10] In working with small quantities, difficulty is sometimes experienced in starting the reaction. In refractory cases, the reaction can often be initiated by the addition of a small quantity of Gilman's magnesium–copper alloy, that has been activated by heating with an equal weight of iodine.

is directly attached to the asymmetric carbon atom) led to a completely inactive anilide.

ITHACA, NEW YORK

PROPARGYL ETHERS OF PHENOL

BY CHARLES D. HURD AND FRANK L. COHEN

In contrast to the considerable information concerning the pyrolysis of allyl aryl ethers,[1] little is known concerning the propargyl aryl ethers. Whereas the former tpye changes on refluxing into o-allylphenols, the latter has been reported[2] to yield nothing but nondescript resins. Thus only tars were found when phenyl propargyl ether or p-bromophenyl propargyl ether was refluxed alone or refluxed in diamyl ether.

For the rearrangement of the propargyl ethers to follow the course of the allyl ethers, the anticipated product would be o-hydroxyphenylallene, rather than o-propargylphenol. It appears to be the gamma carbon of the unsaturated chain which becomes attached to the aromatic nucleus during the rearrangement. Thus, just as $C_6H_5OCH_2CH=C^*H_2$ rearranges into ortho $HOC_6H_4C^*H_2CH=CH_2$, so it might be anticipated that $C_6H_5O-CH_2C\equiv C^*H$ would change into ortho $HOC_6H_4C^*H=C=CH_2$. Furthermore, since 2-methylcoumaran, (A) is a by-product from the pyrolysis of the allyl ether, it might be anticipated that 2-methylcoumaron, (B), would result from the propargyl ether. Both hydroxyphenylallene and methylcoumaron are structures which might be expected to polymerize readily. It is conceivable that either or both of these substances were the precursors of the tar which was noticed from the pyrolysis of propargyl phenyl ether.

In extending this subject we endeavored to synthesize the phenyl ethers of the following propargyl alcohols and to study their pyrolysis:

Triphenylpropargyl alcohol	$C_6H_5C\equiv C-C(C_6H_5)_2OH$
Trimethylpropargyl alcohol	$CH_3C\equiv C-C(CH_3)_2OH$
γ-Methylpropargyl alcohol	$CH_3C\equiv C-CH_2OH$
1-Phenylethinylcyclohexanol-1	$C_6H_5C\equiv C-C(CH_2)_5OH$
α,γ-Diphenyl-α-p-dimethylaminophenylpropargyl alcohol	$C_6H_5C\equiv C-\overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{\displaystyle C_6H_4N(CH_3)_2}{|}}{C}}-OH$

[1] This topic is summarized in Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., New York, 1929, pp. 214–228.

[2] Powell and Adams, THIS JOURNAL, 42, 654 (1920).