2-propyn-1-ol. The 3,5-dinitrobenzoate was prepared from silver 3,5-dinitrobenzoate and it had a melting range of 102–104°. A mixture melting point with the 3,5-dinitrobenzoate (m.p. 102–103.5°) prepared from 2-butyn-1-ol had a melting range of 103–105°.

One part of the chloride and two parts of water were distilled to determine the boiling point of the water azeotrope of the chloride. The azeotrope boiled at 81.5°.

Reaction with Potassium Iodide in Acetone.—The same procedure was used as previously described.[11] The usual modified second order equation, $k = {}^1/_4 bt \log (5 - z)/5(1 - z)$, was used and a plot of $\log (5 - z)/5(1 - z)$ *vs.* time gave a straight line between 25 and 77% reaction for 3-chloro-1-propyne and between 18 and 70% reaction for 1-chloro-2-butyne. The pertinent data are given in Table III.

Reaction with Sodium Ethoxide in Ethanol.—These rates were also determined using a previously described procedure.[12] The usual equation for a bimolecular reaction was used with the molar concentration of 3-chloro-1-propyne being 0.05300 and sodium ethoxide 0.05245, and the molar concentration of 1-chloro-2-butyne being 0.05633 and the sodium ethoxide 0.05605.

A straight line was obtained for 1-chloro-2-butyne between 34 and 67% reaction when $\log b(a - x)/a(b - x)$ was plotted against time. The data obtained for 3-chloro-1-propyne, however, were not amenable to treatment as either a first or second order reaction. The reaction, as measured by hydrochloric acid titration, appeared to approach 60% as a limiting figure. Data for these reactions are given in Table III.

TABLE III

RELATIVE REACTIVITIES OF 3-CHLORO-1-PROPYNE AND 1-CHLORO-2-BUTYNE. POTASSIUM IODIDE IN ACETONE AT 20° AND SODIUM ETHOXIDE IN ETHANOL AT 50°

	Potassium iodide k, hr. mole l.	Sodium ethoxide k, hr. mole l.
3-Chloro-1-propyne	0.279 ± 0.007	[a]
1-Chloro-2-butyne	.419 ± 0.030	2.24 ± 0.04

Cuprous Chloride Catalyzed Acid Hydrolysis at 40°

1-Chloro-2-butyne,						
time, hr.	0.25	0.50	1.00	2.00	3.50	6.00
% reacted	5.8	7.9	10.5	14.7	21.7	36.6

Acid Hydrolysis at 40°

1-Chloro-2-butyne,				
time, hr.	1.00	2.00	3.50	6.00
% reacted	4.1	5.4	2.6	0.0

[a] k values gave a smooth curve from 1.03 for 24% reacted to 0.413 for 60% reacted.

Cuprous Chloride Catalyzed Acid Hydrolysis.—The method of Hatch, Brown and Bailey[13] was used and involved the treatment of 0.0195 mole quantities of the chloride by 50 ml. of 1.5% hydrochloric acid to which had been added 0.00087 mole of cuprous oxide (98%) in one run and no cuprous oxide in another run. Both runs were heated for 3.5 hours at 40° and both showed a small decrease in chloride ion concentration.

The results of catalytic hydrolysis of 1-chloro-2-butyne are given in Table III. This chloride was also treated with a 1.5% hydrochloric acid solution under conditions identical with those used in the catalyzed hydrolysis study but without the added cuprous oxide. The data obtained are also in Table III.

Summary

3-Chloro-1-propyne and 1-chloro-2-butyne have been prepared and characterized. Boiling point data in the literature have been shown to be incorrect.

Reaction of these chlorides with potassium iodide in acetone indicates that a carbon–carbon triple bond increases slightly the reactivity of the chlorine atom in comparison with a carbon–carbon double bond.

1-Chloro-2-butyne reacted more slowly than the crotyl chlorides with sodium ethoxide in ethanol by a factor of about 2.5. This indicates a deactivating influence of the carbon–carbon triple bond for this reaction.

In the reaction between sodium ethoxide in ethanol and 3-chloro-1-propyne there were at least two simultaneous reactions.

1-Chloro-2-butyne was slowly hydrolyzed by a hydrochloric acid solution of cuprous chloride but 3-chloro-1-propyne gave no indication of hydrolysis under the same conditions.

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[11] Hatch, Gordon and Russ, THIS JOURNAL, **70**, 1093 (1948).

[12] Hatch and Alexander, *ibid.*, **71**, 1037 (1949).

[13] Hatch, Brown and Bailey, *ibid.*, **72**, 3198 (1950).

AUSTIN, TEXAS

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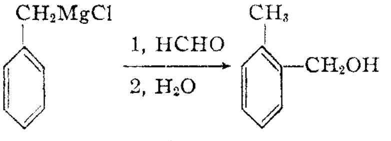
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UTAH STATE AGRICULTURAL COLLEGE]

The Reaction of Benzylmagnesium Halides with Alkyl α-Haloalkyl Ethers[1]

BY LLOYD MALM[2] AND LAWRENCE SUMMERS[3]

Many of the reactions of benzylmagnesium halides yield products in which the entering group becomes attached to the ortho or para carbon atom of the aromatic ring.



With most reactants the rearrangement does not proceed to the exclusion of the "normal" reaction; instead, there is usually obtained a mixture of the ortho-rearranged, para-rearranged and "normal" products. This rearrangement has been the subject of considerable research.[4] However, the publications on this subject have not included any investigation of the effect of regular structural variations in a series of related compounds on the extent of rearrangement. A brief study of this sort is therefore reported here. The reactants chosen were the alkyl α-haloalkyl ethers of the type

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[4] Leading references: Gilman and Kirby, THIS JOURNAL, **54**, 345 (1932); Austin and Johnson, *ibid.*, **54**, 647 (1932); Johnson, *ibid.*, **55**, 3029 (1933). For studies of analogous rearrangements of related types of organometallic compounds see Gilman and Harris, *ibid.*, **49**, 1825 (1927); Gilman and Breuer, *ibid.*, **56**, 1127 (1934); Gilman and Nelson, *ibid.*, **61**, 741 (1939); and the publications of Young and colleagues on the butenyl Grignard reagent, *e.g.*, Young and Roberts *ibid.*, **68**, 1472 (1946).

ROCHXR′ (R = alkyl, X = halogen, R′ = alkyl or hydrogen). Such ethers react cleanly to give mixtures of the ortho, para and "normal" products, and these products are incapable of further reaction with the Grignard reagent. Furthermore, it appears that in these saturated structures the electronic influences must be mainly inductive effects, so that electronic interpretations of the results should be facilitated. The results obtained are shown in Table I.

TABLE I

REACTION OF BENZYLMAGNESIUM HALIDES WITH ALKYL α-HALOALKYL ETHERS

Ether	Grignard	Rearrangement, % of total ether prod. Total	Ortho	Para
CH_3OCH_2Cl	$C_6H_5CH_2MgCl$	12	5	7
$CH_3OCHClCH_3$	$C_6H_5CH_2MgCl$	1	0.8	0.5
$CH_3OCHCl(n\text{-}C_3H_7)$	$C_6H_5CH_2MgCl$	2; 2[a]	2; 2[a]	0; 0[a]
$C_2H_5OCH_2Cl$	$C_6H_5CH_2MgCl$	8	2	6
$n\text{-}C_3H_7OCH_2Cl$	$C_6H_5CH_2MgCl$	5	2.5	2.5
CH_3OCH_2Br	$C_6H_5CH_2MgCl$	21; 22[a]	14; 12[a]	7; 10[a]
CH_3OCH_2I	$C_6H_5CH_2MgCl$	12	6	6
CH_3OCH_2Cl	$C_6H_5CH_2MgBr$	21	13	8
CH_3OCH_2Cl	$C_6H_5CH_2MgI$	16	7	9

[a] Duplicate experiments.

Experimental

Materials.—The benzyl chloride and benzyl bromide were pure commercial chemicals. Benzyl iodide was prepared from benzyl chloride and potassium iodide. The halogen ethers were prepared, according to Henry[5] and Gauthier,[6] from the appropriate alcohol and aldehyde with dry hydrogen chloride. The b.p.'s agreed with the recorded values.

Procedure.—For each run, the Grignard reagent was prepared from 0.1 mole of the benzyl halide and 2.4 g. of magnesium turnings in 60 ml. of ether, with protection from moisture but without the use of an inert atmosphere. The Grignard reagent was filtered through glass wool and was then added dropwise, over a period of 25 minutes, to a solution of 0.1 mole of the halogen ether in 20 ml. of anhydrous ethyl ether, cooled in an ice-bath. The mixture was refluxed for 20 minutes, then 100 ml. of ethyl ether was added and the mixture was hydrolyzed with 100 ml. of cold 10% hydrochloric acid, with ice cooling. The organic layer was washed and dried, and the ethyl ether was removed on a water-bath.

The liquid residue thus obtained was allowed to stand on thin sodium wire for several days, until fresh sodium was unattacked. The liquid was then decanted and distilled. The whole distillate boiling up to about 220° (645 mm.) was taken as the ether fraction. A weighed sample of this material was oxidized with permanganate and the benzoic, phthalic and terephthalic acids were separated by the method of Gilman and Kirby.[4]

Discussion

Johnson[4] has discussed the mechanism of this rearrangement, and Young[4] has investigated at length the rearrangement of the butenyl Grignard reagent. Johnson's formulation shows that there may exist alternate reaction paths by which the same Grignard reagent could give either the normal or rearranged product. It is also of interest to inquire in which case one or the other path will be chosen—that is, what the influence of the structure of the reactant on the mode of reaction will be.

If attention is confined to the total amount of rearrangement, the data of Table I indicate clearly the effect of variations in the groups R or R′ in the structure ROCHXR′. As R was increased from methyl to n-propyl, rearrangement decreased gradually from 12 to 5%. In the position R′, when methyl or n-propyl was substituted for hydrogen, the amount of rearrangement dropped from 12% to 1 or 2%. Presumably the main effect which alkyl groups can exert in these structures is an inductive effect of electron release (relative to hydrogen) toward the reaction center, and this effect appears to facilitate the normal reaction, more sharply when operating on the α-carbon atom than when exerted through the oxygen atom. This is in agreement with previously recorded results,[4] for instance, HCHO gives 100% rearrangement, while CH_3CHO gives none, but $CH_3COOC_2H_5$ again gives some rearrangement. Also CH_3OCH_2Cl gives rearrangement, but CH_3CH_2Cl does not. On this basis empirical predictions as to the probable occurrence of rearrangement can be made—for instance, it can be predicted that the ether $CH_3OC(CH_3)_2Cl$ will give little or none. In fact, if all the literature data on rearrangements of this type with organometallic compounds and various reactants are assembled in tabular form, we find that it is possible empirically to draw a rather distinct boundary line between detectable rearrangement and normal reaction.[7]

The effect of variation of the halogen atom X in the structure ROCHXR′, or in the Grignard reagent, is also shown in Table I. Bromine, in either location, gave the maximum amount of rearrangement, and it is interesting that the same pair of halogens gave about the same results, no matter how they were located—for instance, $C_6H_5CH_2MgCl$ and CH_3OCH_2Br gave the same amount of rearrangement as $C_6H_5CH_2MgBr$ and CH_3OCH_2Cl. More extensive data would be of interest.

In regard to the question of ortho *vs.* para rearrangement neither our data nor any other with which we are familiar offer any basis for generalization.

Summary

The rearrangement reactions of benzylmagnesium halides with some ethers of the type ROCHXR′ (where R = alkyl, R′ = hydrogen or alkyl, and X = halogen) were studied. As R was increased from CH_3 to $n\text{-}C_3H_7$ the percentage of rearrangement decreased gradually. When R′ was changed from H to CH_3 or $n\text{-}C_3H_7$ the percentage of rearrangement dropped sharply. Among the halogens Cl, Br and I, the maximum amount of rearrangement was obtained with Br, whether present in the position X or in the Grignard reagent.

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(5) Henry, *Bull. acad. roy. Belg.*, [3] **25**, 439 (1893); *Ber.*, **26R**, 933 (1893).

(6) Gauthier, *Ann. chim. phys.*, **16**, 289 (1909).

(7) Young, ref. 4, indicates that reactions of Grignard reagents with oxygen and water may be special cases.