Preparation and Thermolysis Reactions of Hydroxytetraarylantimony Compounds

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Eight new hydroxytetraarylantimony compounds, **1**, have been prepared and subjected to thermolysis reactions in *p*-xylene solution. From product ratio data, it has been possible to construct a tentative scale of departure aptitudes of aryl radicals from stiboranyl radicals of the type $XC_6H_4(C_6H_5)_3Sb{-}O\cdot$, **3**, in the propagation steps of induced thermolysis chain reactions. The hydrolysis of pentaphenylantimony in dioxane solution to produce hydroxytetraphenylantimony plus benzene has also been effected, and a preliminary kinetics study of this new reaction has been carried out.

Discussion

Hydroxytetraphenylantimony (**1**, X = H) has been reported[1,2] to undergo decomposition at 50–70 °C, in *p*-xylene solution, under a nitrogen atmosphere, in the dark, to give benzene and triphenylstibine oxide (**2**). A kinetics investigation[3] of this reaction has given results which are consistent with the operation of a radical mechanism in which direct homolytic cleavage of an Sb–C bond is accompanied by an induced radical chain mechanism, a situation analogous to that reported[4,5] for the thermal decomposition of diaroyl peroxides. We have now completed a study of the thermolysis reactions of several compounds of the type $XC_6H_4(C_6H_5)_3SbOH$ (**1**), and the results are summarized in Table I.

Because it was found that many of the triarylstibine oxides (**2** and **4**) underwent decomposition at temperatures above 50 °C, and because the combined yields of C_6H_6 and C_6H_5X were less than quantitative at reaction temperatures of 30–50 °C, even after prolonged reaction periods, it was deemed necessary to determine the material balances in reactions of these types. The results are summarized in Table II. Since all of the material balances given in Table II are close to 100%, the product ratios provided in Table I can be accepted as reasonably accurate measurements of the departure aptitudes of the various aryl groups in the thermolysis reactions. Inasmuch as there are three phenyl groups to one substituted phenyl group in each of the compounds **1**, the significant ratio to be considered is 3 C_6H_5X/C_6H_6. This ratio, corresponding to each of the substituents, X, in **1**, is as follows: *p*-NO_2, 5.6; *m*-NO_2, 9.4; *p*-Cl, 2.5; *m*-Cl, 4.6; *p*-CH_3, 1.3; *m*-CH_3, 0.78; *p*-OCH_3, 2.6; *m*-OCH_3, 2.5.

It is instructive to compare these results with those of known, formally related ionic reactions. Horner, Hoffman, Wippel, and Hassel[6] have determined product ratios in the decomposition reactions of $XC_6H_4(C_6H_5)_3P^+$, OH^-, the product-determining (and rate-limiting)[7] step of which is the dissociation of $XC_6H_4(C_6H_5)_3P{-}O^-$ into a mixture of $(C_6H_5)_3P{=}O + XC_6H_4^-$ and $XC_6H_4(C_6H_5)_2P{=}O + C_6H_5^-$ Each of the aryl anions is immediately converted to the corresponding hydrocarbon by the gain of a proton from the solvent, and perhaps, in some instances, the solvent molecule which donates the proton is even a part of the transition state of the dissociation reaction of the oxyphosphoranyl anion, $XC_6H_4(C_6H_5)_3P{-}O^-$.[8–10] In any event, in this strictly ionic process, it can be inferred from the data of Horner and his co-workers[6] that the decomposition reactions of $XC_6H_4(C_6H_5)_3P^+$, OH^- give the following minimum yields of the predominant aromatic compound (C_6H_5X or C_6H_6): nitrobenzene, 70% (from the *p*-NO_2 salt, i.e., X = *p*-NO_2); nitrobenzene, 100% (X = *m*-NO_2); chlorobenzene, 93% (X = *p*-Cl); benzene, 90% (X = *p*-Me); benzene, 90% (X = *m*-Me); benzene, 87% (X = *p*-MeO); benzene, 90% (X = *m*-MeO). In like manner, the data of McEwen, Briles, and Giddings[11] for the ionic dissociation of $XC_6H_4(C_6H_5)_3Sb(OR)_2^-$ to give mixtures of $(C_6H_5)_3Sb(OR)_2$ + XC_6H_4Na and $XC_6H_4(C_6H_5)_2Sb(OR)_2 + C_6H_5Na$ provide the following departure aptitudes of various aryl anions (which immediately form aromatic hydrocarbons by gain of a proton from the solvent) as calculated from the ratio 3 C_6H_5X/C_6H_6: *p*-$NO_2C_6H_4^-$, >129; *m*-$NO_2C_6H_4^-$, >138; *p*-$CH_3C_6H_4^-$, <0.2; *p*-$CH_3OC_6H_4^-$, <0.75.

All of the data presented above provide further confirmation[3] that the compounds of type **1** undergo thermolysis by radical rather than ionic processes. Although there is only a small degree of discrimination in any of the reactions, it appears that the approximate order of ease of formation of the aryl radicals by the thermolysis of **1** is *m*-nitrophenyl > *p*-nitrophenyl > *m*-chlorophenyl > *p*-chlorophenyl ≃ *p*-methoxyphenyl ≃ *m*-methoxyphenyl > *p*-tolyl > phenyl > *m*-tolyl. The very small difference in the rates of formation of phenyl and *p*-tolyl radicals has been observed repeatedly in the appropriate radical decomposition reactions of triarylsulfonium alkoxides[12–15] and diaryliodonium salts.[16–18] Caserio, Glusker, and Roberts[19] have also reported that, in the hydrolysis of unsymmetrical diaryliodonium salts by a radical mechanism, the direction of cleavage is insensitive to the nature of the substituents. For example, the cleavage of phenyl-*p*-methoxyphenyliodonium salts gives phenol (plus *p*-iodoanisole) in 57–59% yield and *p*-methoxyphenol (plus iodobenzene) in 41–43% yield. Furthermore, the radical hydrolytic cleavage of (*m*-nitrophenyl)-(*p*-methoxyphenyl) iodonium salts gives *p*-methoxyphenol in 47% yield and *m*-nitrophenol in 34% yield.

It is our belief, based on results reported previously,[3] that the major portion of the products of the thermolysis of **1** arise by competing radical chain reactions, the propagation sequences of which are as follows:

$$\underset{3}{XC_6H_4(C_6H_5)_3Sb{-}O\cdot} \rightarrow \underset{4}{XC_6H_4(C_6H_5)_2Sb{=}O} + C_6H_5\cdot$$

$$\underset{1}{XC_6H_4(C_6H_5)_3Sb{-}O{-}H} + C_6H_5\cdot \rightarrow 3 + C_6H_6 \tag{1}$$

$$3 \rightarrow \underset{2}{(C_6H_5)_3Sb{=}O} + XC_6H_4\cdot$$

$$1 + XC_6H_4\cdot \rightarrow 3 + C_6H_5X \tag{2}$$

According to this interpretation, the product ratios 3 C_6H_5X/C_6H_6 given previously are actually a measure of the departure aptitudes of aryl radicals from the intermediate **3** and might have some degree of predictive value in related reactions. Also, as mentioned previously, limited evidence in support of this concept is available in the data on the de-

Table I. Product Ratios in Thermolysis Reactions of $XC_6H_4(C_6H_5)_3SbOH$ (1) in *p*-Xylene

Registry no.	X	Molality of 1	Temp, °C	Time, h	% C_6H_6	% C_6H_5X
61203-18-7	*p*-NO_2	0.0447	35	268	28	52
61203-19-8	*m*-NO_2	0.0447	35	268	14	44
61203-20-1	*p*-Cl	0.0637	35	204	18	15
61203-21-2	*m*-Cl	0.0637	35	204	15	23
61203-22-3	*p*-Me	0.0750	38	238	31	13
61203-23-4	*m*-Me	0.0458	38	238	54	14
61203-24-5	*p*-MeO	0.0258	35	348	28	24
61203-25-6	*m*-MeO	0.0258	35	348	24	20

Table II. Material Balances in Thermolysis Reactions of $XC_6H_4(C_6H_5)_3SbOH$ (1) in *p*-Xylene

X	Concn of 1, mol/10 ml of *p*-xylene	Temp, °C	Time, h	Combined yield of $C_6H_6 + C_6H_5X$, %	Recovered 1, %[a]
p-NO_2	0.00223	35	648	60	43
m-NO_2	0.00223	35	648	50	50
p-Cl	0.00484	25	318	21	72
m-Cl	0.00484	25	318	36	57
p-Me	0.00488	35	318	61	39
m-Me	0.00488	35	318	45	60
p-MeO	0.00253	38	476	40	62
m-MeO	0.00253	38	576	54	40

[a] These numbers are estimated to be accurate within ±7 units.

composition of triarylsulfonium alkoxides[12–15] and diaryliodonium alkoxides.[16,17]

Methods of preparation of tetraarylstibonium salts have been discussed in a previous article.[11] Most of the salts used in the present work were prepared by the reactions of triphenylstibine with aryldiazonium fluoroborates in nitrobenzene solution. The stibonium salts, in turn, were readily converted to the hydroxytetraarylantimony compounds, **1**, by the action of ammonium hydroxide solution.

Although of little practical value at the present time, a theoretically interesting method for the preparation of hydroxytetraarylantimony compounds is by the heretofore unreported hydrolysis of pentaarylantimony compounds. However, the latter are relatively insoluble in water, and they undergo hydrolysis only at a slow rate in an aqueous suspension. In fact, pentaarylantimony compounds are frequently isolated by treatment of a lithium hexaarylantimonate with an excess of water,[20,21] the relatively insoluble Ar_5Sb then being collected by filtration.

Since pentaarylantimony compounds undergo solvolysis fairly rapidly in hydroxylic solvents in which they are soluble,[10,21] it seemed reasonable to attempt the preparation of hydroxytetraphenylantimony by treatment of pentaphenylantimony with 1 equiv of water in a homogeneous solution in an appropriate organic solvent. The use of spectral grade dioxane which had been refluxed over sodium for 24 h and then distilled under an argon atmosphere proved to be suitable for this purpose. In a control experiment, heating of a 0.200 M solution of pentaphenylantimony in the highly purified dioxane for 13 h at 98 °C gave only a trace amount of benzene, as detected by VPC analysis, and pentaphenylantimony was recovered unchanged by evaporation of the solvent. Then, in another experiment carried out under the same conditions, except that exactly 1 equiv of water had been added to the solution, benzene was obtained in 102 ± 3% yield (by VPC analysis). Furthermore, evaporation of the solvent gave a residue of pure hydroxytetraphenylantimony, as determined by its melting point and NMR and IR spectra.[22]

It was also possible to carry out a preliminary kinetics experiment of the reaction of pentaphenylantimony with 1 equiv of water in pure dioxane at 69.7 °C. The reaction was followed for the first 9 h of reaction, which corresponded to 45% of completion. The specific rate constant for the indicated second-order reaction was 1.3×10^{-4} l. mol^{-1} s^{-1}. We believe that the use of pentaphenylantimony for the analysis of water in otherwise inert organic solvents has good potential, and the preliminary rate data are given for the convenience of anyone who might wish to explore this analytical method. It should also work well for the analysis of small amounts of alcohols, carboxylic acids, and other hydroxylic compounds in inert solvents.[10,21]

Experimental Section

General. Melting points and boiling points are uncorrected. NMR spectra were taken on a Varian A-60 instrument. All compounds were dissolved in deuteriochloroform, and Me_4Si was used as an internal standard. GLC analyses were carried out on either a Varian 1200-1 or an F & M 609 flame ionization chromatograph. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., by Alfred Bernhardt Mikroanalytisches Laboratorium, Max Planck Institute, 433 Mulheim (Ruhr), West Germany, and by the late Charles Meade, University of Massachusetts, Amherst, Mass.

Preparation of Aryltriphenylstibonium Fluoroborates. The salts $XC_6H_4Sb^+(C_6H_5)_3, BF_4^-$, in which X = *p*-$NO_2$, *m*-$NO_2$, *p*-Me, and *p*-MeO, were prepared as described previously.[11] With use of nitrobenzene as the solvent, the same method was used to prepare the fluoroborate salts in which X = *m*-Me, *m*-Cl, *p*-Cl, and *m*-MeO. The physical constants of these new salts and preparative data are given in Table III.

Preparation of Hydroxytetraarylantimony Compounds, 1. The dropwise addition of a 10% ammonium hydroxide solution to a stirred solution of 0.005 mol of an aryltriphenylstibonium fluoroborate in about 50–65 ml of acetone and 45–100 ml of water maintained at room temperature gave an immediate precipitate of **1**. The addition of ammondium hydroxide was continued until the mixture became basic to Universal paper. The mixture was then stirred at 0 °C for 5–10 min and filtered, and the precipitate of **1** was washed with cold water, and sometimes subsequently with a small amount of anhydrous acetone. The product was dried in a vacuum desiccator, usually without prior recrystallization. Physical constants of **1** and additional preparative details are provided in Table IV. The melting point hydroxytetra-

Table III. Preparation and Properties of $XC_6H_4Sb^+(C_6H_5)_3$, BF_4^- [a]

Registry no.	X	Mp, °C	Reaction solvent	Reaction temp, °C	Reaction time, h	Recrystn solvent	% yield
61203-27-8	*m*-Me	164–166	Nitrobenzene	90	3	Acetone–ether	35
61203-29-0	*m*-Cl	153–156	Nitrobenzene	60	30	Acetone–ether	30
61203-31-4	*p*-Cl	161–163	Nitrobenzene	80–120	12	Isopropyl alcohol	33
61203-33-6	*m*-MeO	121–125	Nitrobenzene	85	12	Isopropyl alcohol–ether	31

[a] Satisfactory analytical data (±0.3% for C, H, Sb, and halogen) for all compounds were submitted for review.

Table IV. Preparation and Properties of $XC_6H_4Sb(OH)(C_6H_5)_3$, 1 [a]

X	Mp, °C dec	% yield	NMR, δ ($CDCl_3$)
p-NO_2	157–161	82	0.67 s, 7.13–7.97 m
m-NO_2	161–163	79	0.70 s, 7.33–787 m
p-Cl	177–180	57	0.60 s, 7.30–7.90 m
m-Cl	165–170	79	0.70 s, 7.23–7.73 m
p-Me	108–125	48	0.70 s, 2.40 s, 7.10–7.75 m
m-Me	166–168	52	0.77 s, 2.27 s, 7.15–7.85 m
p-MeO	72–75	42	0.77 s, 3.77 s, 7.17–7.83 m
m-MeO	83–106	20	0.60 s, 3.68 s, 7.12–7.80 m

[a] Satisfactory analytical data for all compounds (except as noted) were submitted for review. Exception: X = *p*-Cl. Calcd: C, 59.84; Sb, 25.28. Found: C, 61.08; Sb, 25.80.

phenylantimony was found to be 214–218 °C dec (reported[24,25] mp 210–213 °C dec); NMR δ ($CDCl_3$) 0.80 s (OH), 7.25–7.80 m (aromatic protons). An x-ray crystallographic study of hydroxytetraphenylantimony has been reported.[26]

The procedure described above was entirely satisfactory for the preparation of 1 in which X = H, *p*-NO_2, *m*-NO_2, *p*-Cl, and *m*-Cl, respectively. However, when electron-donating substituents were present (X = *p*-Me, *m*-Me, *p*-MeO, *m*-MeO), a modified procedure had to be employed, one in which a very dilute aqueous solution of the tetraarylstibonium sulfate was treated with ammonium hydroxide. For example, an aqueous solution of 1 (X = *p*-Me, *m*-Me, *p*-MeO, *m*-MeO) sulfate was prepared by heating a mixture of 0.00094 mol of the desired tetraarylstibonium fluoroborate, 150 ml of water (previously distilled from potassium permanganate solution), and 3.0 g of potassium sulfate until most of the stibonium salt had dissolved. The mixture was then cooled and filtered, the precipitate consisting mainly of potassium fluoroborate. Dropwise addition of 10% ammonium hydroxide to the filtrate caused 1 to precipitate, and the addition of NH_4OH was continued until the solution was distinctly basic to Universal paper. The product was collected by filtration, washed well with water, and dried in a vacuum desiccator.

Thermolysis of 1 in *p*-Xylene Solution. A reaction tube was prepared by sealing one end of a 12-in. section of Corning Pyrex special walled glass tubing (o.d. 10 mm, thickness 2 mm). The tube was charged with 1.00 ml of *p*-xylene (previously purged with nitrogen at reflux to remove dissolved oxygen) and sufficient 1 to achieve the molal concentration given in Table I. The reaction tube was sealed under nitrogen, and the reaction mixture, maintained in the dark, was heated at the temperature and for the time period indicated in Table I. The ampules were opened and analyzed for aromatic hydrocarbons by VPC, either a Varian 1200 or an F & M 609 flame ionization instrument being used. For each compound 1, the column packing, column temperature, injection temperature, and detector temperature were as follows: X = *p*-NO_2, 20% Apiezon M on Chromosorb W, 120 °C, 175 °C, 175 °C; X = *m*-NO_2, same as for *p*-NO_2; X = *p*-Cl, 5% polyethylene glycol on Chromosorb W, 90°C, 210 °C, 260 °C; X = *m*-Cl, same as for *p*-Cl; X = *p*-Me, 5% DC 550 on Chromosorb W, 110 °C, 175 °C, 237 °C; X = *m*-Me, *p*-MeO, or *m*-MeO, same as for *p*-Me. Triplicate experiments were carried out for each compound 1, and the average deviation in the values was about ±5%. The values of the unknowns were obtained by comparisons with calibration curves constructed from results determined with known standard solutions. With the compounds, 1, with X = *p*-Cl, *m*-Cl, *p*-Me, *m*-Me, *p*-MeO, and *m*-MeO, not all of the reactant was completely soluble in the *p*-xylene; thus the thermolysis reactions of these compounds were carried out under partially heterogeneous conditions.

Material Balances. The reactions were carried out in the same manner as described above, but under the conditions specified in Table II. After each ampule had been opened, the contents were filtered. The filtrate was analyzed for hydrocarbon content by VPC, essentially as described above. The remaining filtrate was then concentrated to dryness in vacuo, and the gummy residue was induced to solidify by trituration with a small amount of cold pentane. This solid was combined with the original precipitate. An accurately weighed sample of the solid was dissolved in deuteriochloroform and its NMR spectrum taken. The integrated area corresponding to the hydroxyl proton was compared with a calibration curve obtained by use of standard solutions of the particular hydroxytetraarylantimony in order to calculate the amount of unreacted 1 recovered. The data are provided in Table II.

Hydrolysis of Pentaphenylantimony in Dioxane Solution. Dioxane (Mallinckrodt Scintill AR grade) was refluxed over sodium for 24 h and then distilled under argon. All subsequent manipulations and reactions were carried out under an argon atmosphere.

To 0.205 g (4.00×10^{-4} mol) of pentaphenylantimony contained in a 12-mm Pyrex ampule was added 2.00 ml of the purified dioxane. The ampule was sealed under argon and placed in an oil bath maintained at 98.5 °C for 13 h. At the end of this time, the ampule was opened and a 5-μl aliquot was subjected to VPC analysis. No more than a trace of benzene could be detected.

The operation was repeated, except that 7.00×10^{-3} ml (4.00×10^{-4} mol) of water was introduced into the reaction mixture. Following completion of the procedure described above, benzene was found to be present in 102 ± 3% yield, based on the use of a calibration curve constructed from results obtained with known standard solutions of benzene in dioxane. A 0.125-in. Carbowax 20M column was used in this analysis. Evaporation of the dioxane solution to dryness left a residue of nearly pure hydroxytetraphenylantimony, as indicated by its melting point and by its NMR and IR spectra, all of which were identical with the corresponding items of an authentic sample.[24–26]

Preliminary Kinetics Study of the Hydrolysis of Pentaphenylantimony. To 0.205 g (4.00×10^{-4} mol) of pentaphenylantimony contained in a 10-ml Erlenmeyer flask was added 2.00 ml of purified dioxane. The flask was sealed under argon with a rubber septum and placed in an oil bath maintained at 69.7 ± 0.1 °C. After 15 min, 7.0×10^{-3} ml (4.0×10^{-4} mol) of water was introduced through the septum, and aliquots for VPC analysis were withdrawn every 30 min for a 9-h period (corresponding to 45% completion of the reaction). The data provided an excellent fit to the second-order rate law, and the specific rate constant was calculated to be 1.3×10^{-4} l. mol^{-1} s^{-1}.

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Registry No.—$XC_6H_4Sb^+(C_6H_5)_3BF_4^-$ (X = *p*-NO_2), 61203-35-8; $XC_6H_4Sb^+(C_6H_5)_3BF_4^-$ (X = *m*-NO_2), 61203-37-0; $XC_6H_4Sb^+(C_6H_5)_3BF_4^-$ (X = *p*-Me), 61203-39-2; $XC_6H_4Sb^+(C_6H_5)_3BF_4^-$ (X = *p*-MeO), 61203-41-6; $XC_6H_4Sb^+(C_6H_5)_3BF_4^-$ (X = H), 426-80-2; $XC_6H_4(C_6H_5)_3SbOH$ (X = H), 19638-16-5; 1 (X = *p*-Me) sulfate, 61203-42-7; 1 (X = *m*-Me) sulfate, 61203-43-8; 1 (X = *p*-MeO) sulfate, 61203-44-9; 1 (X = *m*-MeO) sulfate, 61203-45-0.

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Attack of Grignard and Lithium Reagents at Carbonyl Oxygens of *o*-Quinol Acetates[1]

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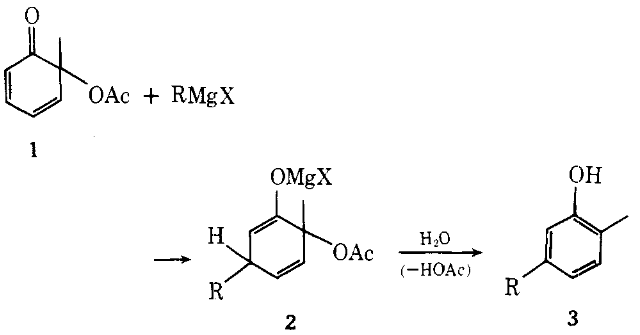
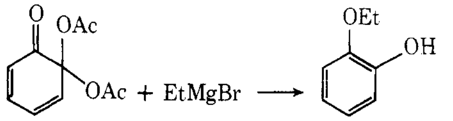
Grignard and lithium reagents react with *o*-quinol acetates (6-acetoxycyclohexa-2,4-dien-1-ones) to give alkyl aryl ethers resulting from formal attack at the "wrong ends" of the ketone carbonyls, as well as the normal reduction products and products arising from 1,2 and 1,4 addition to the conjugated carbonyls. Formation of ethers is not catalyzed by the presence of trace metals, which simply increases the yields of reduction products. Benzyl- and *tert*-butylmagnesium halides give exceptionally high relative yields of ethers, with secondary, primary, and methyl Grignards giving progressively lower yields of ethers. The yields of ethers appear to correlate well with the expected ease of oxidation of the Grignard reagents. These results are explained by assuming initial electron transfer from the organometallic reagent to the quinol acetate, giving a ketyl which then loses an acetate ion to give a phenoxy radical. The ethers are then formed by combination of phenoxy and alkyl radicals. This mechanism explains the occasional formation of 4-alkylphenols, which can arise by reaction of the alkyl radical at C-4 of the phenoxy radical, rather than at oxygen.

In an extensive series of papers, Wessely and his co-workers at the University of Vienna reported that reaction of Grignard reagents (including methyl-, ethyl-, and phenylmagnesium halides) with *o*-quinol acetates (6-acetoxycyclohexa-2,4-dien-1-ones) such as **1** gave 3-alkyl- or 3-arylphenols (e.g., **3**) as well as a variety of products apparently resulting from 1,2 addition of the Grignards to the ketone carbonyl.[2-6] This reaction has appreciable synthetic utility as a method for preparing meta-substituted phenols, which may otherwise be accessible only by multistep paths.[1,7] Formation of meta-substituted phenols presumably proceeds by initial conjugate addition of the Grignard reagent to the unsaturated carbonyls to give intermediates such as **2**, which then lose acetic acid, either during the reaction or during workup, to give **3**.



In one paper, Wessely and Kotlan reported that ethylmagnesium bromide reacted with the quinol diacetate **4** to give the ethyl ether, **5**, as the principal product[3]—a unique example of a Grignard reagent attacking the "wrong end" of a carbonyl group. Similar products were not observed in reactions of other quinol acetates,[2,4-6] while reaction of **4** with methyl- or phenylmagnesium bromides gave good yields of the meta-substituted phenols which should result from "normal" conjugate addition.[3]



4 **5**

While attempting to prepare meta-substituted phenols by reactions of Grignard and lithium reagents with *o*-quinol acetates, we discovered that attack of the carbanionoid reagents at the oxygen atoms of carbonyls to give ethers is a very common result of these reactions.[1,8] This paper discusses the effect of changes in the structures of the organometallic reagents in determining the extent of attack at carbonyl oxygen atoms, and suggests a mechanism for these unusual reactions.

Results

Solutions of Grignard Reagents (1 M, prepared from >99.99% pure magnesium) were added rapidly to equal volumes of solutions of the quinol acetates in ether. To assure