Cyclooctanecarboxylic acid and cyclodecanecarboxylic acid were prepared by carbonation of the cycloalkylmagnesium chlorides with crushed Dry Ice: cyclooctanecarboxylic acid[15] (44%), bp 108° (0.12 mm), and cyclodecanecarboxylic acid[13] (67%), bp 122–123° (0.11 mm), mp 53°.

**Electrolysis of Carboxylic Acids.** The apparatus consisted of a 250-ml electrolytic beaker fitted with a large rubber stopper carrying a thermometer, a Dry Ice finger condenser, and two electrodes. The electrodes were rods 0.55 in. in diameter; the anode was graphite, the cathode, copper. During electrolysis, the mixture was stirred by a magnetic stirrer. The current source was a pair of 85-amp, 12-v batteries in series. A current density of 0.045 $\text{amp/cm}^2$ was maintained for all electrolyses; this current density amounted to 0.8 amp with these electrodes and 100 ml of solution. The current efficiency was approximated by dividing the moles of acid consumed by the faradays of electricity passed as estimated from the volume of gas evolved. Three other cell designs were investigated. A platinum anode was used in place of the graphite one, and a circular copper cathode, perforated to facilitate stirring, was used to allow a uniform field and current density around each anode.

An aqueous mixture consisting of 0.2 mole of cycloalkanecarboxylic acid, 0.075 mole of sodium hydroxide, and enough water to bring the volume to 100 ml was electrolyzed in the cell for 6–8 hr. The mixture was made strongly alkaline with sodium hydroxide, filtered to remove graphite which had crumbled from the anode, and extracted three times with petroleum ether. Cycloalkanecarboxylic acid was recovered from the aqueous layer. The organic extract was dried and distilled. The lower boiling hydrocarbon fraction was easily separated from the higher boiling alcohol and ester products. The hydrocarbon fraction was analyzed by gas chromatography; components in the mixture were identified by comparison of retention times with those of authentic samples and standard mixtures. The data are summarized in Table I. The volume of the gas evolved was measured by its displacement of water and used to compute the current efficiency of the electrolysis.

**Preparation of Authentic Hydrocarbon Samples for Analysis.** *cis*-Bicyclo[*x*.1.0]alkanes were prepared by methyleneation of the corresponding *cis*-cycloalkenes with methylene iodide and zinc–copper couple.[16] The properties were as follows. *cis*-Bicyclo[4.1.0]heptane[16] had bp 115°, $n^{25}\mathrm{D}$ 1.4549; *cis*-bicyclo[6.1.0]nonane[6a] had bp 71–71.5° (26 mm), $n^{25}\mathrm{D}$ 1.4682. *cis*-Bicyclo[7.1.0]decane had bp 83–84° (16 mm), $n^{24}\mathrm{D}$ 1.4740. *Anal.* Calcd for $C_{10}H_{18}$: C, 86.9; H, 13.1. Found: C, 87.05; H, 13.0. The nmr spectrum included multiplet signals centered at 0.4 (1 H), −0.6 (4.4 H), −1.6 (12.6 H), and −1.8 to −2.2 ppm (2 H). *cis*-Bicyclo[8.1.0]undecane had bp 76–77° (5 mm), $n^{25}\mathrm{D}$ 1.4786. *Anal.* Calcd for $C_{11}H_{20}$: C, 86.8; H, 13.2. Found: C, 86.8; H, 13.2. The nmr spectrum included multiplet signals centered at 0.5 (1 H), −0.6 (3.4 H), −1.3 to −1.7 (12.6 H), and −1.9 ppm (3 H).

Bicyclo[4.2.0]octane was prepared by catalytic hydrogenation of bicyclo[4.2.0]oct-7-ene,[17] prepared by photoisomerization of 1,3-cyclooctadiene.[17] The saturated hydrocarbon was obtained with platinum on carbon as catalyst but not with palladium on carbon as catalyst, which apparently isomerized either the bicyclooctene or the bicyclooctane or both. The nmr spectrum of bicyclo[4.2.0]octane includes signals centered at −1.47 (unresolved multiplet, 8 H), −1.82 (quartet with small side bands, 4 H), and −2.32 ppm (unresolved multiplet, 2 H).

*cis*-Cycloheptene and *cis*-cyclooctene were available commercially. A mixture of *cis*- and *trans*-cyclodecene was obtained from Columbian Carbon Co., Lake Charles, La., and another was prepared from cyclodecanol by treatment with *p*-toluenesulfonyl chloride in pyridine solution. A commercial sample of decalin was resolved into *cis* and *trans* isomers by preparative gas chromatography. Mixtures of other hydrocarbons were prepared by decomposition of the appropriate cycloalkanone tosylhydrazones;[6] peak identities in the gas chromatograms were established by reference to literature descriptions of the mixtures.[6]

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[15] M. Godchot and M. Caquil, *Chim. Ind.* (Paris), **29**, 1019 (1933).

[16] H. E. Simmons and R. D. Smith, in *Org. Syn.*, **41**, 72 (1961).

[17] S. F. Chappell, III, and R. F. Clark, *Chem. Ind.* (London), 1198 (1962). A sample of 1,3-cyclooctadiene was generously provided by Columbian Carbon Co., Lake Charles, La.

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# Factors Governing the Reaction of the Benzyl Grignard Reagent. II. Evidence for Triene Intermediates in the Reaction with Chloromethyl Methyl Ether

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*Contribution from the Chemical Laboratories of Purdue University, Lafayette, Indiana 47907.* *Received August 8, 1966*

**Abstract:** The reaction of the benzyl Grignard reagent with chloromethyl methyl ether has been studied in detail. There are at least five major products of this reaction: 2-phenylethyl methyl ether (I), *o*- (II) and *p*-methylbenzyl methyl ether (III), and *o*- (IV) and *p*-(2-methoxyethyl)benzyl methyl ether (V). When tetrahydrofuran is substituted for diethyl ether as a solvent for the reaction, the yield of I is increased and the diethers IV and V are eliminated. The substitution of benzylmagnesium bromide for benzylmagnesium chloride causes an increased yield of II. Benzyllithium forms only compound I in good yield. The major portion of compounds II and III is formed during the hydrolysis step with strong acid (*e.g.*, aqueous HCl). When hydrolysis was effected with ammonium chloride, compounds II and III were virtually eliminated. The intermediate responsible for the formation of II was characterized in part by causing it to react with maleic anhydride and diethyl maleate. Trimethylchlorosilane failed to trap Grignard intermediates which could conceivably function as precursors of the diethers IV and V. Conclusions based on these results were vitiated by the observations that the benzyl Grignard reacts more rapidly with chloromethyl methyl ether than with trimethylchlorosilane. The intermediate responsible for the formation of II could be made to react with gaseous formaldehyde in the presence of anhydrous magnesium chloride in a Prins-type reaction. The same intermediate failed to react with chloromethyl methyl ether under the same conditions.

The benzyl Grignard reagent possesses the intriguing capability of reacting at the α position, to produce so-called "normal" products, as well as at the *ortho* and *para* positions to form "abnormal" products.[1]

In the first paper in this series,[2] it was shown that

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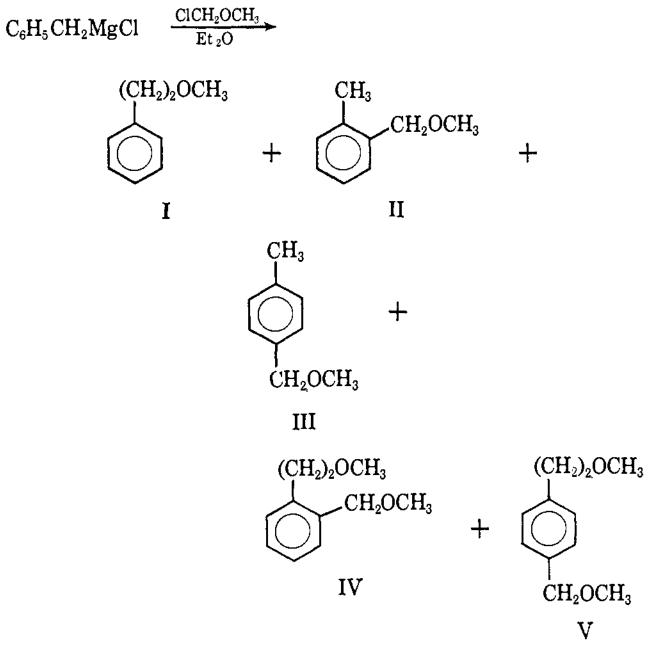
[1] See M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p 1133, for pertinent literature references.

when the benzyl Grignard reacts with acetaldehyde and trifluoroacetaldehyde, only α and *ortho* products are formed but no *para*. In addition, *ortho*-substituted diols are produced in increasing quantities as the concentration of the carbonyl reagent is increased relative to the Grignard. Similar concentration effects had been noted earlier[3] in reactions of the benzyl Grignard with benzaldehyde and citronellal, and mechanisms have been proposed[3b,4] to explain such effects. We now wish to report the results of a study involving a displacement reaction of the benzyl Grignard.

It had been reported[5] that treatment of benzylmagnesium halides with chloromethyl methyl ether produced both *ortho* and *para* coupling products along with the expected α product.

While a careful reexamination has substantiated this earlier report,[5a] several new products have been isolated from this reaction and some new observations made which tend to shed more light on the over-all process and the mechanism whereby it is occurring.

We have found that at least five products are usually produced in the reaction between the benzyl Grignard reagent and chloromethyl methyl ether. The yields of some of these products are dependent to a small extent upon the relative concentrations of the two reactants.



As shown in the equation, in addition to 2-phenylethyl methyl ether (I), *o*-methylbenzyl methyl ether (II), and *p*-methylbenzyl methyl ether (III) already reported,[5a] we have detected varying amounts of the diethers, *o*-(2-methoxyethyl)benzyl methyl ether (IV) and *p*-(2-methoxyethyl)benzyl methyl ether (V). These two latter compounds are new and have never been reported as products of this reaction. The analogy between these diethers and the diols in the case of acetaldehyde and trifluoroacetaldehyde[2] is obvious. It should be noted, however, that with the carbonyl additions,[2] no *para* product corresponding to either III or V was found.

The identification of compounds IV and V was achieved by comparing the infrared spectrum of samples isolated by vapor phase chromatography from the reaction mixture with those obtained from authentic samples (see Experimental Section).

As will be noted from entries 1–4 in Table I, the amounts of IV and V increased slightly as the ratio of the concentration of the chloromethyl methyl ether to Grignard was gradually decreased. At the same time, the percentages of II and III gradually decreased.

**Table I.** Reaction of Benzylmagnesium Halides[a–c] with Chloromethyl Methyl Ether

| Run no. | Grignard: ether ratio | Reaction time, hr | % | | | | |
|---|---|---|---|---|---|---|---|
| | | | I | II | III | IV | V |
| 1 | 3:2 | 3 | 42 | 13 | 12 | Trace | Trace |
| 2 | 1:1 | 3 | 43 | 17 | 10 | 1 | 1 |
| 3 | 1:2 | 3 | 56 | 8 | 6 | 5 | 6 |
| 4 | 1:4 | 3 | 53 | 6 | 6 | 5 | 5 |
| 5 | 1:1 | 0.25 | 42 | 15 | 12 | 0.5 | 0.5 |
| 6 | 1:1 | 24 | 43 | 9 | 10 | 0.5 | 0.5 |
| 7 | 1:1[d] | 3 | 57 | 13 | 6 | 0 | 0 |
| 8 | 1:1[e] | 3 | 36 | 9 | 11 | 3 | 5 |
| 9 | 1:1[f] | 3 | 35 | 8 | 9 | 3 | 5 |
| 10 | 1:1[g] | 3 | 44 | 24 | 9 | Trace | Trace |
| 11 | 1:2[h] | 3 | 63 | 0 | 0 | 0 | 0 |

[a] The initial Grignard concentration was always 0.4 *M*. In all runs except 7, anhydrous diethyl ether was employed as solvent. [b] All reactions listed in this table were hydrolyzed with 15% HCl. [c] In most instances, the percentages listed are the average values for duplicate runs. [d] In this run, THF was used as the solvent. [e] In this run, inverse addition was used, *i.e.*, the Grignard solution was added dropwise *to* the chloromethyl methyl ether. [f] Inverse addition was employed (*i.e.*, same as 8), but 0.3 mole of anhydrous $MgCl_2$ present in ethereal solution containing 0.3 mole of chloromethyl methyl ether. [g] Benzylmagnesium bromide was used in this run instead of the chloride. [h] Benzyllithium was used instead of the Grignard reagent.

An arbitrary reaction time of 3 hr was chosen for the study of concentration effects. A comparison of entries 2 and 5 (Table I) would indicate that this is a very rapid reaction and is almost complete within 15 min. Indeed, a comparison of entries 2 and 6 would indicate that prolonged reaction times (like 24 hr) have a deleterious effect on yield. The amount of compound II in particular seems to drop off in this period. We will return to a discussion of this point later.

At least three other items of interest can be gleaned from the data of Table I. (1) Tetrahydrofuran (entry 7) is a propitious solvent for increasing the rate of α coupling. In this run, the percentage of compound I was 13% higher than when diethyl ether was employed as solvent under otherwise identical conditions. (2) The use of benzylmagnesium bromide (instead of the chloride) increased the amount of compound II produced. The percentages of all other products in the reaction (compare entries 2 and 10, Table I), except for II, are almost identical. (3) The use of benzyllithium instead of the Grignard reagents resulted in an exceed-

(2) R. A. Benkeser and T. E. Johnson, *J. Am. Chem. Soc.*, **88**, 2220 (1966).

(3) (a) J. Schmidlin and A. Garcia-Banus, *Ber.*, **45**, 3193 (1912); (b) W. G. Young and S. Siegel, *J. Am. Chem. Soc.*, **66**, 354 (1944); (c) S. Siegel, S. K. Coburn, and D. R. Levering, *ibid.*, **73**, 3163 (1951).

(4) S. Siegel, W. M. Boyer, and R. R. Jay, *ibid.*, **73**, 3237 (1951).

(5) (a) L. Malm and L. Summers, *ibid.*, **73**, 362 (1951); (b) H. Gilman and J. E. Kirby, *ibid.*, **54**, 345 (1932). See also A. C. Bottomley, A. Lapworth, and A. Walton, *J. Chem. Soc.*, 2215 (1930).

Table II. Reactions of Benzylmagnesium Chloride with Chloromethyl Methyl Ether;[a,b] Reaction Products as a Function of Mode of Hydrolysis

| Run no. | Grignard: ether ratio | Mode of hydrolysis | % I | II | III | IV | V |
|---|---|---|---|---|---|---|---|
| 1 | 1:1 | Aq HCl | 43 | 17 | 10 | 1 | 1 |
| 2 | 1:1 | Aq $NH_4Cl$ | 45 | 1 | 2 | <1 | <1 |

[a] The initial Grignard concentration in each case was 0.4 *M*. The reaction time in each case was 3 hr. The solvent in each case was diethyl ether. [b] The percentages listed are the average values for two runs.

ingly clean reaction (entry 11, Table I) in that only compound I was produced.

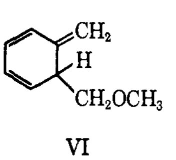
Perhaps the most startling observation was that the product composition (and material balance) was a function of the mode of hydrolysis of the reaction mixture. As depicted in Table II, when the reaction product was hydrolyzed with aqueous hydrochloric acid, rather considerable quantities of II and III were found in the product. On the other hand, when hydrolysis was effected with saturated ammonium chloride, these two products were virtually eliminated. Likewise, the material balance in the latter case was less, owing to the production of a high-boiling residue.

In order to demonstrate even more graphically the difference caused by the hydrolyzing medium, a single reaction mixture was divided into two parts before hydrolysis. One part was hydrolyzed with aqueous hydrochloric acid. This portion produced 12.6 g of product, of which, approximately 64% was I and the remainder a mixture of II and III. The other part was hydrolyzed with a saturated ammonium chloride solution and produced only 10.6 g of product, of which, approximately 93% was compound I and only 7% a mixture of II and III.

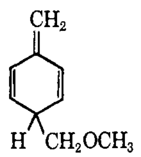
In still another case, an entire reaction mixture was hydrolyzed with a saturated ammonium chloride solution and then worked up in the usual fashion. The dried ethereal extract was then divided into two parts. One part was distilled as usual following solvent removal. The other part was treated with 15% HCl solution in the presence of magnesium chloride (in an attempt to simulate the acid hydrolysis conditions usually used) before distillation. Almost 5 g more of distillable product was obtained in the latter case, comprised largely of *o*- and *p*-methylbenzyl methyl ethers.

These results clearly indicate that a significant portion of compounds II and III *are being formed in the hydrolysis step with aqueous hydrochloric acid.*

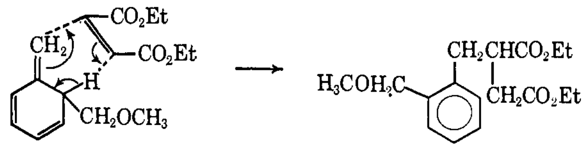
If one assumes that the mechanism for the reaction of the benzyl Grignard with chloromethyl methyl ether is similar to that proposed[6] for its reactions with carbonyl compounds, then triene intermediates like VI and VII might be expected to be present at some point during the reaction.[7] Evidence was obtained for the presence of an intermediate like VI when it was found that maleic anhydride and diethyl maleate would react with a benzylmagnesium chloride–chloromethyl methyl ether reaction mixture before hydrolysis. In the case of diethyl maleate, ethyl α-(*o*-methoxymethyl)benzylsuccinate (VIII) was identified directly as a major product. With maleic anhydride, the α-(*o*-methoxymethyl)benzylsuccinic acid[8] first obtained was also converted by treatment with thionyl chloride and ethanol to ethyl α-(*o*-methoxymethyl)benzylsuccinate (VIII). This product is nicely explained in terms of an "indirect substitutive addition"[9] pictured as occurring *via* a concerted, four-centered, cyclic mechanism.[10-12]



VI



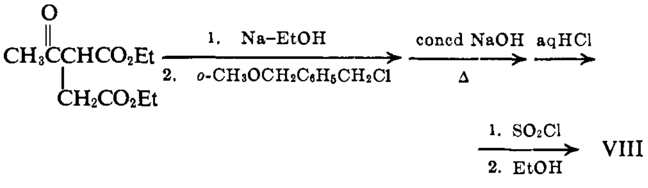
VII



VIII

In fact, it was demonstrated previously[11] that compounds like methylenecyclohexane would react in an analogous manner with maleic anhydride. Of further interest was the observation that only intermediate VI but not VII reacted to any extent with the maleic anhydride or diethyl maleate. This was clearly indicated when work-up of these reaction mixtures, after treatment with maleic anhydride or diethyl maleate, produced none of II, but the usual amounts of III were still present. This result would be anticipated if the cyclic process postulated for these reactions[10,11] was correct. Obviously intermediate VII could not react in this fashion.

Identification of compound VIII was accomplished by matching its infrared spectrum with that of an authentic sample. The latter was prepared by the following sequence.



$$\underset{\text{CH}_2\text{CO}_2\text{Et}}{\text{CH}_3\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CHCO}_2\text{Et}} \xrightarrow[\text{2. }o\text{-CH}_3\text{OCH}_2\text{C}_6\text{H}_5\text{CH}_2\text{Cl}]{\text{1. Na–EtOH}} \xrightarrow[\Delta]{\text{concd NaOH}} \xrightarrow{\text{aqHCl}} \xrightarrow[\text{2. EtOH}]{\text{1. SO}_2\text{Cl}} \text{VIII}$$

In the hope of determining whether the diethers IV and V might be arising through a proton abstraction from intermediates VI and VII by a Grignard base (*e.g.*, $PhCH_2MgX$), followed by reaction with additional chloromethyl methyl ether,[13] an attempt was made to trap the intermediate Grignard reagent (IX or X below)

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[6] J. R. Johnson, *J. Am. Chem. Soc.*, **55**, 3029 (1933). See also W. G. Young and S. Siegel, *ibid.*, **66**, 354 (1944), for a modified version.

[7] Obviously the cyclic mechanism suggested in ref 6 to explain *ortho* products would require modification to explain the formation of *para* products in the present case.

[8] While no particular attempt was made to work with this acid, a sample was isolated from one of the Grignard reaction products with maleic anhydride as a pale yellow solid melting at 140–142°. *Anal.* Calcd for $C_{18}H_{16}O_5$: C, 61.89; H, 6.39. Found: C, 62.23; H, 6.43.

[9] See K. Alder, F. Pascher, and A. Schmitz, *Ber.*, **76**, 27 (1943); K. Alder and H. von Brachel, *Ann.*, **651**, 141 (1962).

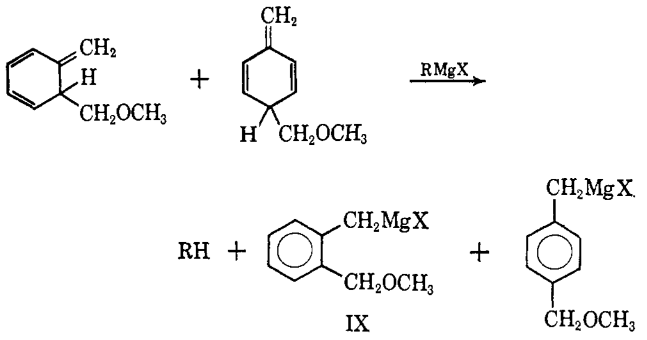
[10] H. P. Koch, *J. Chem. Soc.*, 1111 (1948).

[11] R. T. Arnold and J. F. Dowdall, *J. Am. Chem. Soc.*, 70, 2590 (1948).

[12] R. K. Hill and M. Rabinovitz, *ibid.*, **86**, 965 (1964).

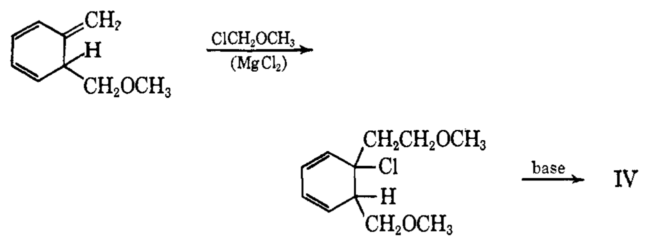
[13] It will be recalled that evidence was obtained (ref 2) that the diols obtained from acetaldehyde were arising, at least in part, *via* this path.

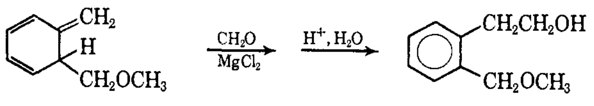
which would be thus formed by causing it to react with trimethylchlorosilane.


IX X

Despite variations in reaction conditions (see Table IV), all such attempts were unsuccessful, and, in no case, could either *o*- or *p*-(methoxymethyl)benzyltrimethylsilane be detected. That these results were not conclusive, however, was shown by a competitive experiment (entry 3, Table IV) between benzylmagnesium chloride, trimethylchlorosilane, and chloromethyl methyl ether. A 65% yield of products resulted from reaction of the Grignard with chloromethyl methyl ether and only a 28% yield of benzyltrimethylsilane despite a 3:1 excess of chlorosilane to chloro ether. Obviously the chloromethyl methyl ether is more reactive toward the benzyl Grignard than toward the chlorosilane.

Another pathway by which diethers like IV and V might possibly arise from intermediates like VI and VII is by a catalyzed addition of chloromethyl methyl ether to the *exo*-methylene group followed by dehydrohalogenation by a base. There is ample precedent for such addition reactions in the literature.[14] To test the possibility that anhydrous magnesium chloride might be functioning as a Lewis acid to catalyze such additions, another reaction between the chloromethyl methyl ether and benzyl Grignard (1:1 mole ratio) was run followed by ammonium chloride hydrolysis. The dried ethereal solution of the product which contained intermediates like VI and VII was divided into two parts. To one portion was added anhydrous magnesium chloride and chloromethyl methyl ethyl; to the other portion was added anhydrous magnesium chloride and gaseous formaldehyde. Both portions were then hydrolyzed with aqueous acid. The quantities of IV and V which were isolated from each of these reactions were identical. This would indicate that the presence of anhydrous magnesium chloride alone is not sufficient to convert VI and/or VII to the diethers IV and/or V. From the formaldehyde reaction, however, a material was isolated by vpc which was shown to be identical with an authentic sample of 2-(*o*-methoxymethyl)phenylethanol (XI). Hence, the well-known Prins reaction[15] had occurred with the *ortho* intermediate and would lend further support to the triene structure VI for this substance.




VI XI

**Conclusions.** The isolation of the diethers IV and V from the reaction with chloromethyl methyl ether might be taken as some indication of the over-all similarity of this reaction to that with acetaldehyde and trifluoroacetaldehyde[2] wherein *o*-diol products were produced. On the other hand, with the carbonyl reagents no trace of *para* products were found while, in the present case, *para* products (III and V) usually constituted 10–15% of the product. Additional work will be needed to provide a rationale for this difference.

For the first time, unequivocal evidence is presented which shows that the "abnormal" products of this reaction (*i.e.*, compounds II and III) arise principally during the hydrolysis step with aqueous acid. While we have no direct evidence to date (*e.g.*, spectral data) for the structures of the intermediates leading to II and III, we feel the structures represented by VI and VII are likely candidates. Such compounds might be expected to undergo the Prins reaction with formaldehyde, to react with maleic anhydride and diethyl maleate, and to be aromatized by strong acid. In addition, it would seem likely that such reactive intermediates (particularly VI) might deteriorate over prolonged reaction times, possibly owing to polymerization. This would explain the lower yield of II which we observed over a 24-hr reaction period (entry 6, Table I).

The significance of our inability to trap intermediate Grignard species like IX or X which could act as precursors to the diether products observed (IV and V) was obviously vitiated by our findings with regard to the relative reactivity of the benzyl Grignard toward chloromethyl methyl ether and trimethylchlorosilane. Species like IX and X could still be responsible for the formation of IV and V. Likewise, our success in bringing about a Prins reaction with gaseous formaldehyde and intermediate VI sheds little light on the present case.[16] This is particularly true when chloromethyl methyl ether failed to react with intermediate VI in the presence of anhydrous magnesium chloride. One could rationalize (perhaps incorrectly) the failure of this latter reaction by the assumption that a base is needed (like the benzyl Grignard) to effect the dehydrohalogenation of an intermediate chloro ether–olefin adduct. Unfortunately, attempts to test this hypothesis by adding more magnesium chloride to the reaction mixture and reversing the mode of addition of the reagents (entries 8 and 9, Table I) were not successful. Obviously, there is an interplay of variables operative

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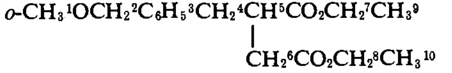
[14] F. Straus and W. Thiel, *Ann.*, **525**, 151 (1936); C. D. Nenitzescu and V. Przemetzki, *Ber.*, **69**, 2706 (1936); **74**, 676 (1941). See also N. D. Scott, U. S. Patent 2,024,749 (Dec 17, 1935); *Chem. Abstr.*, **30**, 1067 (1936).

[15] E. Arundale and L. A. Mikeska, *Chem. Rev.*, **51**, 505 (1952).

[16] It does, however, provide an interesting possibility for the formation of *o*-(2-hydroxyethyl)benzyl alcohol in the reaction between the benzyl Grignard and formaldehyde.

**Table III.** Nmr Spectra of Various Methyl Ethers[a]

| Methyl ether | $\tau$ values[b] |
|---|---|
| $C_6H_5{}^1CH_2{}^2CH_2{}^3OCH_3{}^4$ | 2.80 ($H^1$, m), 7.22 ($H^2$, t), 6.52 ($H^3$, t), 6.77 ($H^4$, s) |
| $o$-$CH_3{}^1C_6H_4{}^2CH_2{}^3OCH_3{}^4$ | 7.73 ($H^1$, s), 2.84 ($H^2$, m), 5.67 ($H^3$, s), 6.72 ($H^4$, s) |
| $m$-$CH_3{}^1C_6H_4{}^2CH_2{}^3OCH_3{}^4$ | 7.70 ($H^1$, s), 3.00 ($H^2$, m), 5.71 ($H^3$, s), 6.74 ($H^4$, s) |
| $p$-$CH_3{}^1C_6H_4{}^2CH_2{}^3OCH_3{}^4$ | 7.70 ($H^1$, s), 2.94 ($H^2$, m), 5.70 ($H^3$, s), 6.76 (H,$^4$ s) |
| $o$-$CH_3{}^1OCH_2{}^2C_6H_4{}^3CH_2{}^4CH_2{}^5OCH_3{}^6$ | 6.70 ($H^1$, s), 5.58 ($H^2$, s), 2.80 ($H^3$, m), 7.15 ($H^4$, t), 6.50 ($H^5$, m), 6.75 ($H^6$, s) |
| $p$-$CH_3{}^1OCH_2{}^2C_6H_4{}^3CH_2{}^4CH_2{}^5OCH_3{}^6$ | 6.70 ($H^1$, $H^6$, s), 5.62 ($H^2$, s), 2.79 ($H^3$, m), 7.18 ($H^4$, t), 6.47 ($H^5$, t) |
| $o$-$CH_3{}^1OCH_2{}^2C_6H_4{}^3CH_2{}^4Si(CH_3{}^5)_3$* | 6.62 ($H^1$, s), 5.62 ($H^2$, s), 2.92 ($H^3$, m), 7.80 ($H^4$, s), 9.92 ($H^5$, s) |
| $p$-$CH_3{}^1OCH_2{}^2C_6H_4{}^3CH_2{}^4Si(CH_3{}^5)_3$* | 6.60 ($H^1$, s), 5.57 ($H^2$, s), 2.90 ($H^3$, q), 7.82 ($H^4$, s), 9.88 ($H^5$, s) |
|  $o$-$CH_3{}^1OCH_2{}^2C_6H_5{}^3CH_2{}^4CH^5(CH_2{}^6CO_2CH_2{}^8CH_3{}^{10})CO_2CH_2{}^7CH_3{}^9$ | 6.67 ($H^1$, s), 5.57 ($H^2$, s), 2.83 ($H^3$, m), 7.10 ($H^4$, $H^5$, m), 7.57 ($H^6$, complex pattern), 5.97 ($H^7$, $H^8$, q), 8.82 ($H^9$, $H^{10}$, overlapping t) |

[a] All spectra were determined in carbon tetrachloride solution using tetramethylsilane as internal standard, except for the asterisked compounds where methylene chloride was used as the internal standard. A Varian A-60 nmr spectrometer was employed. Chemical shifts are measured from the estimated center of a singlet or multiplet. In the case of each spectra listed, the peak areas are quite consistent with the proton assignments made. [b] Abbreviations used are: m, multiplet; t, triplet; s, singlet; q, quartet.

here that will require further experimentation to unravel.

## Experimental Section

**Part I.** In this part are listed the preparations of all new compounds which it was necessary to synthesize and characterize during the course of this problem.

***m*-Methylbenzyl Methyl Ether.** This compound was prepared in conventional fashion from 7.0 g (0.3 g-atom) of sodium, 20.0 g (0.164 mole) of *m*-tolylcarbinol,[17] and 42.5 g (0.3 mole) of methyl iodide. A 54% yield (12.0 g) of product was obtained, bp 68–70° (7.5 mm).

A sample was obtained by vpc collection using a 6 ft × 0.25 in. stainless steel column packed with 20% Zonyl E-7 and 10% Bentone-34 on 60–80 mesh, AW/DMCS Chromosorb[18] W at 150°. An infrared and nmr spectrum (see Table III) both confirmed the structure.

*Anal.* Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.45; H, 8.94.

***o*-(2-Methoxyethyl)benzyl Methyl Ether.** This compound was prepared from 25 g (0.165 mole) of *o*-(2-hydroxyethyl)benzyl alcohol,[19] 9 g (0.39 g-atom) of sodium, and 71 g (0.5 mole) of methyl iodide. A 29% yield (8.5 g) of product was obtained, bp 65–66° (0.25 mm).

A sample was obtained by vpc collection using a 6 ft × 0.25 in. stainless steel column packed with 20% FFAP on 60–80 mesh, AW/HMDS treated Chromosorb W[18] at 175°. An infrared and nmr spectrum confirmed its structure.

*Anal.* Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.34; H, 9.17.

***p*-(2-Methoxyethyl)benzyl Methyl Ether.** This compound was prepared in 38% yield by essentially the same method described above for the *ortho* compound except for the use of *p*-(2-hydroxyethyl)benzyl alcohol.[20] The compound boiled at 73–78° (0.25 mm). An infrared and nmr spectrum (Table III) taken on a sample collected by vpc (same column as for the *ortho* isomer) confirmed its structure.

*Anal.* Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.18; H, 9.11.

***o*-(Methoxymethyl)benzyltrimethylsilane.** In a 500-ml, three-necked flask fitted with a ground-glass stirrer, reflux condenser, and addition funnel was placed 6.1 g (0.25 g-atom) of magnesium powder. The entire system was flamed out while it was being flushed with dry nitrogen. All subsequent operations were carried out under nitrogen.

The magnesium was covered with 100 ml of freshly distilled THF (from $LiAlH_4$), and a mixture of 25 g (0.125 mole) of *o*-chlorobenzyltrimethylsilane[21] and 13.6 g (0.125 mole) of ethyl bromide was added to the magnesium over 30 min. The mixture was refluxed 10 hr.

The black mixture was cooled, and 25 g (0.31 mole) of chloromethyl methyl ether was added as rapidly as possible. The mixture was refluxed for 14 hr, then 100 ml of ethyl ether was added, followed by immediate hydrolysis with 15% HCl solution. After the usual work-up, there was obtained 13.8 g (53%) of product, bp 63–65° (0.4 mm). Redistillation yielded 10 g of material, bp 62° (0.2 mm).

An infrared and nmr spectrum (Table III) was obtained on a sample collected by vpc (5 ft × 0.25 in. stainless steel column packed with 20% silicone oil on 60–80 mesh firebrick at 165°).

*Anal.* Calcd for $C_{12}H_{20}OSi$: C, 69.17; H, 9.68. Found: C, 69.48; H, 9.79.

***p*-(Methoxymethyl)benzyltrimethylsilane.** This compound was prepared in a very similar fashion to that described above for the *ortho* isomer except for the use of *p*-chlorobenzyltrimethylsilane.[21] There was obtained 17.5 g of product, bp 76–80° (0.6 mm). Redistillation yielded 9.2 g (35%) of material, bp 62–63° (0.25 mm).

An infrared and nmr spectrum (Table III) obtained on a sample collected by vpc (Zonyl E-7–Bentone-34, 165°) confirmed its structure.

*Anal.* Calcd for $C_{12}H_{20}OSi$: C, 69.17; H, 9.68. Found: C, 69.11; H, 9.50.

**Ethyl $\alpha$-(*o*-Methoxymethyl)benzylsuccinate.** A solution of 1.5 g (0.065 g-atom) of sodium in 100 ml of absolute ethanol was prepared in a 500-ml, three-necked flask equipped with a ground-glass stirrer and reflux condenser. To this solution was added 25 g (0.116 mole) of ethyl $\alpha$-acetosuccinate.[22] The orange solution was stirred for 1 hr at room temperature, and then 10 g (0.058 mole) of *o*-(methoxymethyl)benzyl chloride[23] in 25 ml of absolute ethanol was added slowly. The mixture was refluxed until it was no longer basic to hydrion paper (4 hr).

The ethanol was removed by distillation, and, after a solution of 24 g (0.6 mole) of NaOH in 100 ml of water was added, the mixture was refluxed for 16.5 hr. It was then poured on ice and neutralized with HCl solution, followed by extraction with ethyl ether. After removal of the ether, a dark red oil was deposited.

The red oil was dissolved in 100 ml of acetone, filtered, and then diluted with 50 ml of benzene. The solution was concentrated, and then 100 ml more of benzene was added.

The benzene solution (a solid had gradually appeared in this solution) was treated with 50 ml of thionyl chloride and then refluxed for 7 hr. The excess thionyl chloride was removed by distillation, and then 75 ml of absolute ethanol was added followed by a 12-hr refluxing period.

The ethanol was removed, and the residue was distilled. An orange distillate, which contained a pale yellow solid, was collected, bp 140–170° (0.6 mm). This distillate was dissolved in ether, filtered, and redistilled [bp 160–165° (0.6 mm)]. Column chromatography on alumina with petroleum ether (35–37°) as eluent gave 5.3 g of residue after solvent removal. Analysis of this material by vpc (5% FFAP column at 230°) showed only one major com-

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(17) *Org. Reactions*, **6**, 504 (1951). This compound was prepared by $LiAlH_4$ reduction of *m*-toluic acid.

(18) This stationary phase was purchased from Wilkens Instrument and Research, Walnut Creek, Calif.

(19) S. Siegel and S. Coburn, *J. Am. Chem. Soc.*, **73**, 5494 (1951). This compound was prepared by the $LiAlH_4$ reduction of homophthalic acid using the technique of R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 2548 (1947), for ether-insoluble acids.

(20) This compound was prepared in essentially the same manner as the *ortho* isomer from homoterephthalic acid, mp 62–63°. *Anal.* Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.22; H, 7.96.

(21) C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 939 (1954).

(22) H. Adkins, N. Isbell, and B. Wojcik, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc. New York, N. Y., 1943, p 262.

(23) F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 2819 (1954).

ponent. An infrared and nmr spectrum on a sample collected by vpc confirmed its structure.

*Anal.* Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.85. Found: C, 66.11; H, 7.71.

**Part II. Benzyl Organometallics. a. Benzylmagnesium Chloride.** In a 1-l., three-necked flask equipped with a ground-glass stirrer, addition funnel, and reflux condenser was placed 77.8 g (3.2 g-atoms) of magnesium turnings. The entire system was flamed out while it was being flushed with dry nitrogen. All subsequent operations were carried out under a nitrogen atmosphere. The magnesium was covered with 180 ml of anhydrous ethyl ether, and a solution of 101.2 g (0.8 mole) of benzyl chloride in 270 ml of anhydrous ethyl ether was placed in the addition funnel. A small portion of this solution was added to the magnesium to initiate the reaction, and then the remainder was added slowly over a period of 3–4 hr. The mixture was stirred for 0.5 hr after the addition was complete.

The yields of benzylmagnesium chloride by this method were consistently in the range of 88–98% as determined by hydrolysis of an aliquot in standard acid followed by back-titration with standard base.

b. **Benzylmagnesium Bromide.** This preparation was identical in every respect with that described above for the chloride except that the benzyl bromide addition required 5–6 hr. The yield of benzylmagnesium bromide (determined by titration as described above) was about 87%.

c. **Benzyllithium.** This preparation was carried out using 21.4 g (0.05 mole) of tribenzyltin chloride[24] in 100 ml of anhydrous ethyl ether and 0.21 mole of an ethereal solution of methyllithium in essential accordance with the directions of Seyferth.[25]

**Benzylmagnesium Halides and Chloromethyl Methyl Ether.** All reactions listed in Table I (except entry 11) were carried out in a similar fashion. The directions given below for entry 2, Table I, can be taken as generally typical of all runs.

A solution of benzylmagnesium chloride in ethyl ether was prepared in 88% yield as described above. A 0.4 *M* solution of this Grignard reagent was prepared in a dry, 2-l., three-necked flask equipped with a ground-glass stirrer, reflux condenser (fitted with a "Drierite" drying tube), and addition funnel by diluting the appropriate volume of Grignard solution (in this case, 190 ml, 0.3 mole) to a volume of 750 ml with anhydrous ethyl ether. A solution of 24.1 g (0.3 mole) of chloromethyl methyl ether[26] in 50 ml of anhydrous ethyl ether was added to the Grignard solution over 15 min. The mixture was stirred for 3 hr at room temperature after the addition was complete.

The mixture was hydrolyzed by the careful addition of 100 ml of 15% hydrochloric acid followed by 100 ml of water. The two layers were separated, and the aqueous layer was washed twice with 80-ml portions of ethyl ether. The combined ether extracts were dried over anhydrous $K_2CO_3$.

After solvent removal (12 in. Vigreux column), the residue was distilled and the following fractions were collected: a, 1.7 g (2.1 g),[27] bp 50° (100 mm); b, 28.9 g (27.0 g), bp 60–70° (6 mm); c, 4.3 g (4.6 g), bp 60–145° (0.5 mm). Some tarry residue remained in the distillation flask.

All fractions were analyzed by vpc (F & M Model 500 chromatograph with a glass liner in the injection port). Fraction a was found to be toluene (20 ft × 1/8 in. stainless steel column packed with 2.5% di-*n*-butyl tetrachlorophthalate and 2.5% Bentone-34 on 80–100 mesh, AW/HMDS treated Chromosorb W at 140°), and the ethyl ether distillate was also found to contain some toluene. Fraction b (same analytical column as above) was found to contain 2-phenylethyl methyl ether,[28] *p*-methylbenzyl methyl ether,[29] and *o*-methylbenzyl methyl ether[29] (elution in that order). Samples of each of these three compounds were collected by vpc (6 ft × 0.25 in. stainless steel column, 20% Zonyl E-7 and 10% Bentone-34 on 60–80 mesh, AW/DMCS treated Chromosorb W at 120°), and their infrared spectra shown to be identical with those of authentic samples. Fraction c was redistilled to give 2.0 g (2.8 g in duplicate run) of product boiling from room temperature to 80° (0.2 mm) and 1.7 g of residue (0.9 g in duplicate run). Analysis by vpc (5 ft × 0.25 in. stainless steel column packed with 5% FFAP on 60–80 mesh, AW/DMCS treated Chromosorb G at 150°) showed this fraction contained traces of the three compounds found in b, several unknown components, benzyl alcohol, and bibenzyl. The two major unknown peaks were collected and shown to have identical infrared and nmr spectra as authentic samples of *o*- and *p*-(2-methoxyethyl)benzyl methyl ethers (see above for preparation).

An attempt was made to analyze the residue by vpc, but it was a complex mixture which could not be completely separated.

Table I, entry 2, gives a composite of the analytical results for this run.

**Benzyllithium and Chloromethyl Methyl Ether. (Entry 11, Table I).** The benzyllithium solution prepared as described above was diluted with ethyl ether to a volume of 375 ml.[30] A solution of 24.1 g (0.3 mole) of chloromethyl methyl ether in 50 ml of anhydrous ethyl ether was added over 15 min. The mixture was stirred for 3 hr at room temperature.

All other details of work-up and analysis are identical with those described above for the benzylmagnesium halide runs.

**Benzylmagnesium Chloride and Chloromethyl Methyl Ether. Attempted Trapping of Intermediate with Trimethylchlorosilane.** A typical reaction as described above was run using 0.3 mole of Grignard and 0.3 mole of chloromethyl methyl ether. After the customary reaction time of 3 hr, 65.2 g (0.6 mole) of trimethylchlorosilane was added, and the mixture was stirred for 20 hr at room temperature.

Hydrolysis, work-up, and analytical method were identical with that described above. The average results for duplicate runs are listed as entry 1, Table IV. No components with the same retention times of authentic samples of *o*- or *p*-(methoxymethyl)benzyltrimethylsilane could be found.

**Table IV.** Reaction of Benzylmagnesium Chloride with Chloromethyl Methyl Ether; Trapping Experiments with Trimethylchlorosilane[a,b]

| Run no. | Grignard: ether ratio | Reaction time, hr | % I | II | III | IV | V |
|---|---|---|---|---|---|---|---|
| 1 | 1:1 | 3[c] | 39 | 5 | 6 | 3 | 3 |
| 2 | 1:1 | 0.25[d] | 42 | 7 | 10 | 2 | 3 |
| 3 | 3:2 | ...[e] | 44 | 9 | 10 | 1 | 1 |

[a] The values listed in this table are the average of duplicate runs. [b] In both runs 1 and 2 above, there was isolated in each case a 2% yield of benzyltrimethylsilane. In run 3, a 28% yield of benzyltrimethylsilane was obtained. [c] The chloromethyl methyl ether was allowed to react with the Grignard for 3 hr before the trimethylchlorosilane was added. The resulting mixture was then stirred at room temperature for 20 hr. [d] After a 0.25-hr reaction time between the Grignard and the chloromethyl methyl ether, the trimethylchlorosilane was added. This mixture was then stirred at room temperature for 24 hr. [e] In this run, the trimethylchlorosilane (0.6 mole) was added at the same time as the chloromethyl methyl ether (0.2 mole), followed by a 20-hr reaction at room temperature.

The above experiment was repeated in duplicate (see entry 2, Table IV) except that the trimethylchlorosilane (0.6 mole) was added immediately *after* the addition (15 min) of the chloromethyl methyl ether. The entire mixture was then stirred for 24 hr at room temperature. Again, no evidence was found for *o*- or *p*-(methoxymethyl)benzyltrimethylsilane.

**Competitive Reaction between Benzylmagnesium Chloride–Chloromethyl Methyl Ether and Trimethylchlorosilane.** To the usual Grignard solution containing 0.3 mole of benzylmagnesium chloride in 750 ml of anhydrous ethyl ether was added a mixture of 16.1 g (0.2 mole) of chloromethyl methyl ether and 65.2 g (0.6 mole) of trimethylchlorosilane over a 20-min period. The resulting mixture was then stirred for 20 hr at room temperature.

The average results of duplicate experiments are listed as entry 3 in Table IV. No evidence for the presence of *o*- or *p*-(methoxymethyl)benzyltrimethylsilane was found.

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(24) K. Sisido and Z. Kinugawa, Japan Patent 6626 (1953); K. Sisido, Y. Takeda, and Z. Kinugawa, *J. Am. Chem. Soc.*, **83**, 538 (1961).

(25) D. Seyferth, R. Suzuki, C. J. Murphy, and C. R. Sabet, *J. Organometal. Chem.* (Amsterdam), 2, 431 (1964).

(26) C. S. Marvel and P. K. Porter "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 377.

(27) The values in parentheses are the results of a duplicate run.

(28) S. Mamedov and D. N. Khydyrov, *Zh. Obshch. Khim.*, **32**, 1427 (1962); *Chem. Abstr.*, **58**, 4453*e* (1963).

(29) C. D. Gutsche and H. E. Johnson, *J. Am. Chem. Soc.*, 77, 109 (1955).

(30) Based on a theoretical yield of benzyllithium, this dilution would produce a 0.4 *M* solution containing 0.15 mole of benzyllithium.

**Benzylmagnesium Chloride and Chloromethyl Methyl Ether. Addition of Maleic Anhydride and Diethyl Maleate.** An ethereal solution (750 ml) containing 0.3 mole of benzylmagnesium chloride was prepared in the usual way. A solution of 0.3 mole of chloromethyl methyl ether in 50 ml of ether was added over 15 min, and the mixture was stirred for 1 hr at room temperature. To this was carefully added 29.4 g (0.3 mole) of maleic anhydride. The resulting pale yellow mixture was stirred for 24 hr at room temperature.

The mixture was hydrolyzed with 100 ml of 15% HCl solution, and then 100 ml of water was added followed by the usual work-up. The ether solution was extracted three times with 100-ml portions of NaOH solution (50 g/600 ml of $H_2O$) giving a red solution. The ether solution (A) was dried over anhydrous $K_2CO_3$.

The NaOH solution was neutralized with 15% HCl to produce an insoluble red oil. After extraction with ether and drying with sodium sulfate, the ether solution (B) was filtered and solvent removed whereupon a yellow solid was deposited. A portion of this yellow solid (15 g) was added to 100 ml of thionyl chloride and refluxed for 3 hr. After removal of the excess thionyl chloride by distillation, the residue was dissolved in 100 ml of absolute ethanol and refluxed for 17.5 hr. The ethanol was removed and the residue distilled to give 12 g of a yellow liquid, bp 100–160° (0.3 mm). Redistillation yielded 6.8 g of a pale yellow liquid, bp 145–150° (0.3 mm).

Analysis by vpc (5 ft × 0.25 in. stainless steel column containing 5% FFAP on 60–80 mesh, AW/DMCS treated Chromosorb G at 225°) showed one major component. A sample was purified by vpc. Its infrared and nmr spectra were identical with those of an authentic sample of ethyl $\alpha$-(*o*-methoxymethyl)benzylsuccinate (see above).

*Anal.* Calcd for $C_{17}H_{25}O_5$: C, 66.21; H, 7.85; mol wt, 308. Found: C, 66.36; H, 7.62; mol wt, 305.

The solvent was removed from the ether solution (A above) of the reaction mixture and the residue distilled as described previously. Analysis by vpc (usual conditions) indicated the following yields: 2-phenylethyl methyl ether, 39%; *p*-methylbenzyl methyl ether, 8%; *o*-(2-methoxyethyl)benzyl methyl ether, 0.5%; and *p*-(2-methoxyethyl)benzyl methyl ether, 0.5%. No *o*-methylbenzyl methyl ether was found.

The above reaction was repeated in every detail except that 51.6 g (0.3 mole) of diethyl maleate was added instead of the maleic anhydride. Following the usual hydrolysis and work-up, distillation produced a forerun consisting of the usual 2-phenylethyl methyl ether, *p*-methylbenzyl methyl ether, and trace quantities of *o*- and *p*-(2-methoxyethyl)benzyl methyl ethers. There was then collected 21.5 g of a cut, bp 140–155° (0.25 mm), which, by vpc was shown to be largely ethyl $\alpha$-(*o*-methoxymethyl)benzylsuccinate. An infrared spectrum of a sample collected by vpc from this cut was identical with that of an authentic sample.

**Benzylmagnesium Chloride and Chloromethyl Methyl Ether. Effect of Aqueous HCl *vs.* $NH_4Cl$ Hydrolysis.** The usual 1:1 mole ratio of benzyl Grignard and chloromethyl methyl ether was employed. All reaction conditions were identical with those previously described except that hydrolysis was effected with 100 ml of saturated ammonium chloride solution instead of the aqueous hydrochloric acid. The results obtained are listed as entry 2 in Table II.

In another run, the reaction mixture was divided into two parts *before* hydrolysis. One part was hydrolyzed with 50 ml of 15% HCl followed by 50 ml of water and the other by 50 ml of saturated $NH_4Cl$ and 50 ml of water. The usual work-up and analysis gave the results shown in Table V.

In yet another experiment, the reaction mixture was hydrolyzed with saturated ammonium chloride followed by the usual work-up. The ethyl ether extracts were dried over $K_2CO_3$ and then divided into two parts.

Table V

| Compound | $NH_4Cl$, g | HCl, g |
|---|---|---|
| 2-Phenylethyl methyl ether | 9.9 | 8.0 |
| *o*-Methylbenzyl methyl ether | 0.3 | 3.2 |
| *p*-Methylbenzyl methyl ether | 0.4 | 1.4 |
| Total | 10.6 | 12.6 |

One part was worked up as usual. The other part was treated with 100 ml of 15% HCl solution in the presence of anhydrous magnesium chloride (10.0 g) and heated for 0.5 hr. The usual work-up followed. The analyses gave the results shown in Table VI.

Table VI

| Compound | $NH_4Cl$ only, g | $NH_4Cl$ plus HCl, g |
|---|---|---|
| 2-Phenylethyl methyl ether | 8.7 | 7.5 |
| *o*-Methylbenzyl methyl ether | 0.2 | 3.8 |
| *p*-Methylbenzyl methyl ether | 0.4 | 2.8 |
| Total | 9.3 | 14.1 |

**Benzylmagnesium Chloride and Chloromethyl Methyl Ether. Ammonium Chloride Hydrolysis Followed by Reaction with Gaseous Formaldehyde and Chloromethyl Methyl Ether.** The usual reaction with a 1:1 mole ratio of benzyl Grignard to chloromethyl methyl ether was carried out. Hydrolysis was effected with saturated ammonium chloride solution, and the usual work-up followed. The ethyl ether extracts were dried over $K_2CO_3$ and then divided into two parts.

One part of the ether solution was placed in a 1-l., three-necked flask equipped with a ground-glass stirrer and Dry Ice condenser. To this was added 5 g of anhydrous $MgCl_2$ followed by 22.5 g (0.75 mole) of gaseous formaldehyde[31] over 45 min. The mixture was stirred for 3 hr at room temperature and then hydrolyzed with 100 ml of 15% HCl. The usual work-up and analysis followed.

The other part of the ether solution from the reaction was placed in a 1-l., three-necked flask equipped with a ground-glass stirrer, reflux condenser, and addition funnel. To this was added 5 g of anhydrous $MgCl_2$ followed by a solution of 24.1 g (0.3 mole) of chloromethyl methyl ether in 50 ml of ether. The mixture was refluxed for 3 hr, then hydrolyzed with 100 ml of 15% HCl solution followed by 100 ml of water. The usual work-up and analysis followed.

Compounds I–V were present in almost identical quantities in both of the above experiments. In addition, a sample was isolated by vpc (5 ft × 0.25 in., 5% FFAP column at 190°) from the formaldehyde reaction whose infrared spectrum was identical with that of an authentic sample of 2-(*o*-methoxymethyl)phenylethanol.[32]

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[31] J. F. Walker, "Formaldehyde," Reinhold Publishing Corp., New York, N. Y., 1964, p 46.

[32] F. G. Holliman and F. G. Mann, *J. Chem. Soc.*, 1634 (1947).