dominantly of acetone and that fraction (56 g.), b.p. 79–83° at 20 mm., contains 38 g. of cyclohexylcarbinol and 16 g. of isopropyl ester of cyclohexanecarboxylic acid.

Reaction between Ethylene, CO and Methanol.—One hundred and twenty-eight grams of methanol, 4 g. of Raney cobalt, 43 g. of ethylene and carbon monoxide up to a pressure of 250 atm. are charged into a rocking autoclave of 1700-ml. capacity. The agitation is started and the autoclave is heated to 200°. The temperature is held at 200–205° for 8 hr., during which time the pressure drops from 470 to 405 atm. After cooling, 250 l. of gas (ethylene 2.5%) and 181 g. of liquid containing suspended metallic cobalt are obtained. By fractional distillation, 3 g. of propionaldehyde, 21 g. of methyl propionate and 27.5 g. of diethyl ketone are obtained.

Reaction between Ethylene, CO and 2-Butanol.—Two hundred and ten grams of 2-butanol, 4 g. of Raney cobalt, 110 g. of ethylene and carbon monoxide up to a pressure of 170 atm. are charged to the autoclave described above. The agitation is started and the autoclave is heated to 210°. The temperature is held at 207–210° for 9 hr., during which time the pressure drops from 355 to 275 atm. After cooling, 195 l. of gas (ethylene 18%) and 306 g. of liquid containing metallic cobalt in suspension are taken off. Fractional distillation of 299 g. of decanted liquid, followed by analytical determination shows that 55 g. of methyl ethyl ketone and 68 g. of diethyl ketone are obtained.

Reaction between Propylene, CO and Aniline.—Three hundred and ten grams of aniline, 13 g. of propylene and 3 g. of Raney cobalt are introduced in an autoclave of 435 ml. capacity. Carbon monoxide is then introduced up to a pressure of 250 atm. The agitation is started and the autoclave is heated to 170° and held at this temperature for 5 hr. After cooling, 335 g. of products are discharged, and, after filtration, the unaltered aniline (250 g.) is distilled at 20 mm. The remaining products are distilled at 0.8 mm. 28 g. of aniline and 41 g. of a mixture of *n*- and isobutyranilide are obtained.

Reaction between Styrene, CO and Aniline.—Sixty-nine grams of aniline, 61.6 g. of freshly redistilled styrene and 2.4 g. of Raney cobalt are put into a 435-ml. autoclave. Carbon monoxide is then introduced up to a pressure of 250 atm. The agitation is started and the autoclave is heated to 200° and held at this temperature for 6 hr. After cooling, 127 g. of a mixture of solid and liquid compounds are discharged. The products are filtered and 45 g. of diphenylurea separated as a white precipitate. The precipitate is washed with ether and the washing liquid is added to the filtrate. After removal of ether by rectification, the liquid products are distilled and two fractions are collected. The first fraction (24 g.), b.p. 112–160°, is accurately rectified and yields 13 g. of ethylbenzene, $n^{20}D$ 1.4960. The second fraction (16 g.), b.p. 75–80° at 20 mm. , is mostly aniline. The residue (50 g.) is then distilled at 0.5 mm.: the fraction boiling at 180–210° (19.4 g.), after several recrystallizations from ligroin, yields pure β-phenylpropionanilide, m.p. 97–98°.

Reaction between Methyl Crotonate, CO and Aniline.—Ninety-three grams of aniline, 60 g. of methyl crotonate and 1 g. of cobalt on kieselguhr are put into a 435-ml. autoclave. Carbon monoxide is then introduced to a pressure of 180 atm. The agitation is started and the autoclave is heated to 200° and held at this temperature for 6 hr. After cooling, 165 g. of liquid products is discharged. The catalyst is separated by filtration and the unreacted aniline (64 g.) and methyl crotonate (40 g.) are distilled off under reduced pressure, the residue dissolved in ligroin, the solution decolorized with bone charcoal and concentrated. On standing, methylsuccinic acid dianilide (30 g.) crystallizes.

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Reactions of Haloalkyl Ethers with Phenyllithium[1]

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Phenyllithium may react with haloalkyl ethers to cause displacement of halogen by phenyl, dehydrohalogenation, or halogen-metal interconversion. The nature and position of the halogen atom determine which type of reaction will predominate. With γ-haloalkyl ethers, the yield of the product of displacement of halogen by phenyl increased in the order Cl < Br < I, and the amount of dehydrohalogenation decreased in the order Cl > Br or I. With the β-halogen compounds, halogen–metal interconversion occurred with iodine or bromine (I ≫ Br), but the γ-halogen ethers gave essentially no halogen–metal interconversion, even when the halogen was iodine. In the case of α-chloroalkyl ethers the expected displacement of halogen by phenyl occurred.

The reactions which have been reported in the literature as occurring with halogen-substituted alkyl ethers and active organometallic compounds (usually Grignard reagents) are of three types; (1) displacement of halogen on carbon, (2) elimination of the elements of HX or (3) displacement of carbon on halogen ("halogen–metal interconversion"). Besides these, reactions involving cleavage of C–O bonds by the RM compound may occur, either simultaneously or subsequently. This paper reports some experiments which indicate that when the organometallic compound is phenyllithium all three of the above types of reactions can be realized, and that the nature and position of the halogen atom determine which type of reaction will predominate. The results obtained are shown in Table I.

The reaction of α-haloalkyl ethers with Grignard reagents[2] has been applied extensively in the past. A similar reaction for organolithium compounds has not been reported, perhaps because the use of a lithium compound offers no apparent advantages for preparative purposes. This type of reaction was found to proceed satisfactorily with phenyllithium and α-chloroalkyl ethers at room temperature.

Although reactions of type 1 are quite broad in scope, they cannot be used to prepare ethers such as 1-methoxy-2-phenylethane from benzylmagnesium halides and chloromethyl ethers, because of the occurrence of rearrangement.[3] It was thought possible that organolithium compounds, which are sometimes more active in displacement reactions than are Grignard reagents, might react well enough with β-haloalkyl ethers to make the synthesis of such β-substituted ethers in this fashion practical. The reaction of phenyllithium with one equivalent of 1-methoxy-2-chloroethane, however, gave 74% of benzene and only a trace of

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[1] This work was supported in part by a Frederick Gardner Cottrell grant from the Research Corporation.

[2] L. L. Hamonet, *Bull. soc. chim.*, [4] **3**, 254 (1908).

[3] H. Gilman and J. E. Kirby, THIS JOURNAL, **54**, 345 (1932); L. Malm and L. Summers, *ibid.*, **73**, 362 (1951).

TABLE I

REACTIONS OF HALOALKYL ETHERS WITH PHENYLLITHIUM

Ether	Mole used	C_6H_6	Product (% yield)			
			Coupling		Interconversion	
$CH_3OCHClCH_3$	0.25	[a]	$CH_3OCH(C_6H_5)CH_3$	55	.....	
$CH_3OCH_2CH_2Cl$	.25	74	$CH_3OCH_2CH_2C_6H_5$	0.3	.....	
$C_2H_5OCH_2CH_2Cl$	.23	46	$C_2H_5OCH_2CH_2C_6H_5$	0.1	.....	
$CH_3OCH_2CH_2Br$	.27	13	$CH_3OCH_2CH_2C_6H_5$	22	C_6H_5Br	<12[b]
$CH_3OCH_2CH_2Br$[c]	[c]	..	$CH_3OCH_2CH_2C_6H_5$	33[d]	.....	
$CH_3OCH_2CH_2Br$[e]	[e]	..	$CH_3OCH_2CH_2C_6H_5$	47[d]	.....	
$C_2H_5OCH_2CH_2Br$	0.25	17	$C_2H_5OCH_2CH_2C_6H_5$	36	C_6H_5Br	<13
$CH_3OCH_2CH_2I$	.13	[f]	$CH_3OCH_2CH_2C_6H_5$	[f]	C_6H_5I	71[g,h]
$C_2H_5OCHClCH_2Cl$[i]	.25	37	$C_2H_5OC(C_6H_5){:}CH_2$	25	.....	
$C_2H_5OCH_2CH_2CH_2Cl$	.21[j]	[j]	$C_2H_5OCH_2CH_2CH_2C_6H_5$	5	.....	
$C_2H_5OCH_2CH_2CH_2Cl$[k]	.18	21	$C_2H_5OCH_2CH_2CH_2C_6H_5$	14	.....	
$C_2H_5OCH_2CH_2CH_2Br$	.23	15	$C_2H_5OCH_2CH_2CH_2C_6H_5$	42	[l]	
$C_2H_5OCH_2CH_2CH_2I$	.18	15	$C_2H_5OCH_2CH_2CH_2C_6H_5$	58	[m]	

[a] Used phenyllithium in slight excess, recovered 1.0 g. of benzene. [b] No ethylene could be detected. [c] Treated 0.33 mole of halo ether with 0.22 mole of phenyllithium while heating at reflux. [d] Based on phenyllithium. [e] Treated 0.33 mole of halo ether with 0.22 mole of phenyllithium at temperature of ice-bath. [f] None could be isolated. [g] Wittig, ref. 4, reports 84%. [h] Ethylene, 8%, isolated as the dibromide. [i] Used 0.50 mole of phenyllithium. [j] The phenyllithium did not react completely, as shown by a color test. [k] Refluxed 3.5 hours at 39°. [l] Trace of bromobenzene present. [m] Trace of iodobenzene present.

1-methoxy-2-phenylethane—that is, the reaction proceeded almost entirely by elimination. 1-Ethoxy-2-chloroethane reacted similarly. β-Bromoethyl ethers did give up to 36% of the desired β-phenylethyl compounds (plus approximately 15% benzene). Finally, as reported by Wittig[4] in the only previous literature reference to the reaction of an organolithium compound with a haloalkyl ether, 1-methoxy-2-iodoethane reacts with phenyllithium to give iodobenzene in good yield (type 3). Examination of the products of our reactions involving the β-bromoethyl ethers showed that here, also, some bromobenzene resulted.

The α-chloro ethers, then, gave the expected coupling reaction, the β-chloro ethers gave elimination, the β-bromo ethers predominantly coupling, and the β-iodo compounds halogen–metal interconversion. These reactions can be combined, in appropriate cases, to accomplish in one procedure a preparation usually carried out in more than one step. Thus 1-ethoxy-1,2-dichloroethane, with two equivalents of phenyllithium, gave 25% of 1-ethoxy-1-phenylethene. The two-step process[5] gives a higher over-all yield of this compound. However, in the studies reported here we did not attempt to establish conditions for optimum yields, but instead to obtain comparison data on the nature of the reactions when the same conditions were maintained in each case. We did investigate briefly other conditions for the reaction of 1-methoxy-2-bromoethane with phenyllithium, and found that the yield of 1-methoxy-2-phenylethane could be increased from 22 to 47% by appropriate changes in temperature and concentrations.

As was expected, γ-chloroalkyl ethers were less reactive than the β-chloro compounds. Under the conditions used in the other studies, phenyllithium did not react completely with 1-ethoxy-3-chloropropane, and the reaction yielded only 5% of 1-ethoxy-3-phenylpropane. Refluxing the mixture for 3.5 hours caused the phenyllithium to react, and gave 1-ethoxy-3-phenylpropane (14%) and benzene (21%). (In this as in some of the other cases, the discrepancy in the material balance may probably be attributed to ether-cleavage reactions of the type mentioned above.) With γ-bromoalkyl ethers the phenyllithium reacted completely at room temperature, and the yield of coupling product increased to 42%. With γ-iodoalkyl ethers there was a still further increase, to give 58% yield of 1-ethoxy-3-phenylpropane. Halogen–metal interconversion was suggested only by a small trace of iodobenzene; no cyclopropane could be isolated.

The rather marked change in the nature of the reaction according to the nature and position of the halogen atom is interesting. Such reactions as these are presumably the result of attack on the haloalkyl ether by some active anion in the phenyllithium solution, and a realistic discussion of the mechanism would depend on a knowledge of the nature[6] of this anion.

Experimental

Materials.—The phenyllithium solutions, about 1 *M*, were prepared as usual[7] in diethyl ether, and were titrated to determine the exact concentrations. All reactions involving phenyllithium were carried out under dry nitrogen.

1-Methoxy-1-chloroethane,[8a] 1-methoxy-2-chloroethane,[8b] 1-ethoxy-2-chloroethane,[8c] 1-methoxy-2-bromoethane,[8d] 1-ethoxy-2-bromoethane,[8e] 1-methoxy-2-iodoethane,[8f] 1-ethoxy-3-chloropropane,[8g] 1-ethoxy-3-bromopropane[8c] and 1-ethoxy-3-iodopropane[8h] were prepared by previously described methods. Their physical constants agreed with the reported values.

The 1-ethoxy-1,2-dichloroethane was a redistilled Eastman Kodak Co. material.

General Procedure.—Except where otherwise specifically noted in Table I, the reactions were carried out as follows: The amount of phenyllithium used was exactly one mole per

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(4) G. Wittig and G. Harborth, *Ber.*, **77**, 306 (1944).

(5) W. M. Lauer and M. A. Spielman, THIS JOURNAL, **55**, 4923 (1933).

(6) See for instance G. Wittig, *Z. angew. Chem.*, **62**, 231 (1950).

(7) R. G. Jones and H. Gilman, *Organic Reactions*, **6**, 363 (1951).

(8) (a) H. R. Henze and J. T. Murchison, THIS JOURNAL, **53**, 4077 (1931); (b) G. M. Bennett and F. Heathcoat, *J. Chem. Soc.*, **132**, 268 (1929); (c) C. D. Hurd and G. W. Fowler, THIS JOURNAL, **61**, 249 (1939); (d) prepared by method of ref. 8e; (e) G. C. Harrison and H Diehl, *Org. Syntheses*, **23**, 32 (1943); (f) L. W. Jones and D. H. Powers, THIS JOURNAL, **46**, 2518 (1924); (g) L. I. Smith and J. A. Sprung, *ibid.*, **65**, 1276 (1943); (h) prepared by method of ref. 8f.

mole of haloalkyl ether. The required volume of phenyllithium solution was added from a calibrated dropping funnel, over a period of 1.5 hours, to the haloalkyl ether in solution in 50 ml. of diethyl ether. Mechanical stirring was employed, and addition was at room temperature without cooling. The reactions proceeded smoothly, with mild refluxing. The Michler ketone color test[9] was negative a the end of the addition (except in the case of 1-ethoxy-3-chloropropane), indicating absence of phenyllithium. Occasional color tests made during the course of the addition indicated that reaction was immediate, since such tests were always negative. The reaction mixture was cooled in an ice-bath and hydrolyzed by the addition of aqueous ammonium chloride. After separation, washing with water, and drying on Drierite, the organic layer was distilled. A 42-cm. Fenske column ($^1/_8$-in. glass helices) was used to separate the diethyl ether, benzene, and other low-boiling products. The higher-boiling portion was then distilled under reduced pressure through a 25-cm. Vigreux column.

For certain reactions, data not apparent from Table I are given below.

1-Methoxy-1-chloroethane.—The 1-methoxy-1-phenylethane had b.p. 54–57° (11 mm.), n^{20}D 1.4918; the reported[10] b.p. is 55–57° (11 mm.). For derivatization, a sample of 8 g. of this product was converted to the iodide by 12 hours of refluxing with 80 ml. of 47% hydriodic acid, and the iodide was identified[11] as the S-alkylisothiouronium picrate, m.p. 168–169°.

1-Methoxy-2-bromoethane.—The reaction apparatus was attached to a series of three gas-washing bottles, each containing a solution of bromine in carbon tetrachloride. After the reaction was completed the apparatus was flushed out with nitrogen, while still connected to the absorption train. The contents of the gas-washing bottles were then washed with sodium bisulfite solution and with water, separated, dried on Drierite, and distilled to recover any ethylene dibromide. None was found in this case. However, the distillation of the main reaction mixture yielded 5.0 g. of an impure fraction, b.p. 40–66° (10 mm.), which contained some bromobenzene, as shown by its conversion, through the Grignard reagent, to benzoic acid, m.p. 122°.

The 1-methoxy-2-phenylethane, b.p. 66–70° (10 mm.), n^{21}D 1.5001, reported[12] b.p. 70–74° (12 mm.), had the characteristic sweet odor. A 7-g. sample was converted to 1-iodo-2-phenylethane by boiling for 11 hours with 80 ml. of 47% hydriodic acid, and the iodo compound was derivatized as the S-alkylisothiouronium picrate,[11] m.p. 138–139°.

In other experiments, as shown in Table I, the conditions of this reaction were varied in order to improve the yield. The best result was obtained when 0.22 mole of phenyllithium in about 200 ml. of ethyl ether was added slowly to 0.33 mole (50% excess) of 1-methoxy-2-bromoethane in 90 ml. of ethyl ether, cooled and stirred in an ice-bath.

1-Ethoxy-2-bromoethane.—Bromobenzene and 1-ethoxy-2-phenylethane, b.p. 78–79° (10 mm.), n^{20}D 1.4976, reported[13] b.p. 198–199° and n^{32}D 1.4870, were identified as indicated above. The presence of ethylene was not investigated.

1-Methoxy-2-iodoethane.—The procedure described above was used for the detection of ethylene. The ethylene dibromide, b.p. 130–134°, obtained by distillation of the product from the gas-washing bottles, was characterized as the S-alkylisothiouronium picrate,[11] identified by m.p. (259–260°) and mixed m.p. with an authentic specimen.

1-Ethoxy-1,2-dichloroethane.—In this reaction two moles of phenyllithium was used per mole of haloalkyl ether. The 1-ethoxy-1-phenylethene, b.p. 93–98° (18 mm.), n^{20}D 1.5299, reported[5] b.p. 109–112° (30 mm.) and $n^{25.5}$D 1.5287, was hydrolyzed by heating with alcoholic hydrochloric acid.[5] The resulting acetophenone was converted to the semicarbazone, which was identified by m.p. (198–199°) and mixed m.p. with an authentic specimen.

1-Ethoxy-3-chloropropane.—When this reaction was carried out under the above conditions, reaction was much slower than in the case of the α- or β-haloalkyl ethers. The color test[9] was strongly positive at the end of the addition, and the final products included benzene in 34% yield. This is not shown in Table I, since it could have come mostly from unreacted phenyllithium. The 1-ethoxy-3-phenylpropane was converted to the iodide as above, and the latter was identified by converting it to the Grignard reagent and then carbonating with solid carbon dioxide, to give 3-phenylbutyric acid, m.p. 47–48°.

The reaction was repeated as above, except that after addition was complete the mixture was refluxed until a negative color test was obtained (3.5 hours). This treatment increased the yield of the coupling product, 1-ethoxy-3-phenylpropane, b.p. 90–95° (10 mm.), n^{23}D 1.4938, reported[14] b.p. 85–90° (20 mm.).

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(10) W. Reppe, O. Schichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

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Polymethylbenzene Complexes of Iodine and Iodine Monochloride

BY L. J. ANDREWS AND R. M. KEEFER

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Previous studies of halogen–aromatic interactions have been extended using modified procedures to include several of the polymethylbenzenes. The relative magnitudes of the equilibrium constants for the formation of 1:1 complexes with iodine or iodine monochloride of the various methylated benzenes have been found to parallel in general the tendency of the aromatic substances to undergo interaction with hydrogen fluoride–boron trifluoride solutions. Equilibrium constants for the interaction of iodine monochloride with ethyl-, isopropyl- and *t*-butylbenzene were also measured and were found to be, within close limits, the same as that for toluene. Theoretical aspects of these findings have been considered.

The generalization that increasing methyl substitution enhances the basic character of the aromatic nucleus is best illustrated by the work of McCaulay and Lien.[1] These investigators have observed that, with certain exceptions, the tendency for methylbenzenes to form complexes of the type $ArH^+BF_4^-$ in hydrogen fluoride–boron trifluoride solutions increases as the number of ring methyl substituents increases from one to six. A similar order of stability has been shown to apply to the benzene, toluene and xylene complexes of silver ion,[2] bromine,[3] iodine monochloride[4] and sulfur dioxide.[5] The mesitylene–iodine complex is more stable than that of benzene and iodine.[6] However, with silver ion mesitylene[7] yields a complex which is less stable than that formed by benz-

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