Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.13; H, 10.23.

The 2,4-dinitrophenylhydrazine derivative[21] was crystallized from ethyl acetate-ethanol, m.p. 195.4–196.6°.

Anal. Calcd. for $C_{21}H_{24}N_8O_8$: C, 48.83; H, 4.68; N, 21.70. Found: C, 49.09; H, 4.78; N, 21.84.

Benzyl chloride and 2,4-pentanedione. Benzyl chloride, 63.2 g. (0.5 mole) was added during 20 min., with cooling as necessary, to a stirred slurry of sodium hydride, 12 g. (0.5 mole) and 2,4-pentanedione, 26 g. (0.25 mole) in 100 ml. of dimethyl sulfoxide. After 2.5 hr. the solution was still basic, but after an additional 1 hr. on a steam bath it was neutral. The solution was cooled and poured into 125 ml. of water. The top layer was dissolved in 500 ml. of ether and then filtered. The aqueous solution was extracted once with 100 ml. of ether and the combined organic solutions were washed with two 50-ml. portions of water. The solvent was evaporated to about 200 ml., 100 ml. of petroleum ether (b.p. 60–68°) was added, and the solution was put in a refrigerator over night. The buff solid, 14 g. (20%), was collected and after crystallization from a mixture of 100 ml. of petroleum ether and 75 ml. of benzene and then from pure petroleum ether, it had a m.p. of 113.2–113.4° (lit.,[23] m.p., 111–112°).

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.35; H, 7.17. Found: C, 81.57; H, 7.24.

The 2,4-dinitrophenylhydrazine derivative[21] was crystallized from ethyl acetate, m.p. 252.0–253.5° dec.

Anal. Calcd. for $C_{31}H_{28}N_8O_8$: C, 58.12; H, 4.40; N, 17.50. Found: C, 58.28; H, 4.36; N, 17.00.

Cooling of the mother liquors at −80° gave another 1.8 g. (2.5%), m.p. 83–110°. The solvent was evaporated and the residue fractionated at 0.1 mm. to give six fractions: (1) b.p. 27–40°, 6.2 g., two components by vapor phase chromatography in the ratio of 1:3.4; (2) b.p. 40–78°, 1.0 g.; (3) b.p. 78–84°, 8.3 g., n_D^{24} 1.5308, vapor phase chromatography shows a small amount of the two components of the first fraction plus larger amounts of three other components; (4) b.p. 84–103°, 1.8 g., n_D^{24} 1.5363; (5) b.p. 103–125°, 6.6 g., n_D^{24} 1.5531[24] and (6) b.p. 125–140°, 0.8 g. There was a considerable quantity of a viscous orange polymeric material left in the pot.

By distillation at atmospheric pressure, infrared and vapor phase chromatography comparisons, the first fraction was determined to consist of a mixture of benzyl alcohol and benzyl acetate. No ketonic or aldehydic material was detected in this fraction. Fractions 3 and 4 were combined and treated with saturated copper(II) acetate solution to give the slate gray copper chelate of 3-benzyl-2,4-pentanedione, m.p. 203–205° (lit.,[25] m.p., 205–207°). A portion of the original fraction 3 was converted into the 2,4-dinitrophenylhydrazine derivative[21] of 3-benzyl-2,4-pentanedione which crystallized from ethyl acetate–ethyl alcohol as a bright red powder, m.p. 200.3–202.0°.

Anal. Calcd. for $C_{24}H_{22}N_8O_8$: C, 52.36; H, 4.03; N, 20.36. Found: C, 52.75; H, 4.12; N, 19.93.

The fifth fraction crystallized from pentane at −80° but melted too rapidly to allow collection. It was identified as 1,1-dibenzylacetone by its 2,4-dinitrophenylhydrazine derivative,[21] orange needles from alcohol, m.p. 124.6–125.8° (lit.,[26] m.p. 126–127°).

Anal. Calcd. for $C_{23}H_{22}N_4O_4$: C, 66.01; H, 5.30; N, 13.39. Found: C, 66.04; H, 5.46; N, 13.36, and by its infrared spectrum,[17] 1711 cm.$^{-1}$, C=O; 1456, 1370–1355 cm.$^{-1}$, —CH_3.

The other components of the reaction were not identified but it was possible to estimate yields of about 17% and 11%, respectively, for the monobenzyl-2,4-pentanedione and the dibenzylacetone from the vapor phase chromatography curves.

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[23] G. T. Morgan and C. J. A. Taylor, *J. Chem. Soc.*, **127**, 797 (1925). These authors reported an over-all yield of about 12% based on alkylation of $NaCH(COCH_3)_2$ with benzyl chloride (39%) followed by alkylation of $(C_6H_5CH_2)CNa(COCH_3)_2$ with benzyl chloride (30%).

[24] J. M. Conia, *Ann. Chem.* [*Paris*], **8**, 709 (1953), gives a b.p. of 192–194°/15 mm. and n_D^{21} 1.5543 for 1,1-dibenzylacetone.

[25] C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

[26] R. A. Barnes and B. D. Beitchman, *J. Am. Chem. Soc.*, **76**, 5430 (1954).

Formation of Some Organometallic Compounds in Phenyl Ether

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A recent publication[1] reports that an attempt to prepare *n*-amylmagnesium bromide using phenyl ether as the solvent did not give the expected compounds, but instead there occurred a Friedel-Crafts reaction to give a coupling product. Grignard reagents have been prepared in various solvents.[2] Evans and Diepenhorst,[3] in studies of the photoluminescence of Grignard reagents, prepared the Grignard reagents of *o*-bromoanisole and of 2-bromocymene in phenyl ether, but did not give yields or experimental details. They may have used "special catalysts" as well as "heating for several hours in sealed tubes."

A difficulty which is present in the formation of organometallic compounds in the presence of aryl ethers is a tendency for metalation of the ether. Challenger and Miller[4] report that Grignard reagents in the presence of anisole and phenetole at elevated temperatures effect metalation of the ethers in the *ortho*-position in low yields. Dibenzofuran, a derivative of phenyl ether, is metalated by ethylmagnesium bromide in the 4-position.[5] The metalation of phenyl ether is effected much more readily with organolithium compounds.[6]

In the course of an investigation of the preparation of organolithium compounds in phenyl ether, it was observed that *n*-butyllithium does form, but the extent to which it forms and then metalates the solvent reduces its usefulness. Methyllithium and phenyllithium apparently did not form

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[1] G. S. Handler, *J. Org. Chem.*, **24**, 1339 (1959).

[2] M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, Inc., New York, N. Y., 1954, pp. 45–53.

[3] W. V. Evans and E. M. Diepenhorst, *J. Am. Chem. Soc.*, **48**, 715 (1926).

[4] F. Challenger and S. Miller, *J. Chem. Soc.*, 894 (1938).

[5] H. Gilman and A. Haubein, *J. Am. Chem. Soc.*, **67**, 1033 (1945).

[6] K. Oita and H. Gilman, *J. Am. Chem. Soc.*, **79**, 339 (1957). See also, H. Gilman and S. Gray, *J. Org. Chem.*, **23**, 1476 (1958).

TABLE I

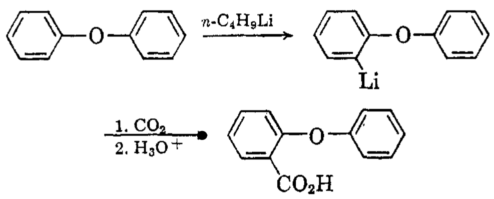
REACTION OF *n*-BUTYL BROMIDE WITH LITHIUM IN PHENYL ETHER FOLLOWED BY CARBONATION

Run	Lithium, G.-atom	*n*-Butyl Bromide, Mole	Phenyl Ether, Mole	Reaction Time, Hr.	Conditions	*o*-Phenoxybenzoic Acid, %	Valeric Acid, %
1	0.25	0.125	0.50	112	50°[a]	12.6	—
2	0.512	0.265	0.50	48	R.T.[a]	3.34	Trace[c]
3	0.690	0.125	0.50	5	R.T.[b]	3.06	7.82
4	0.275	0.0625	0.50	26	R.T.[b]	13.4	—

[a] *n*-Butyl bromide was added dropwise to a suspension of finely cut lithium wire in phenyl ether. [b] Lithium was added portionwise to a solution of *n*-butyl bromide in phenyl ether. [c] Valeric acid identified by means of its *p*-toluidide, m.p. and mixed m.p. 73–74°.

under corresponding conditions. Carbonation of the reaction mixtures led to either mixtures of valeric acid and *o*-phenoxybenzoic acid or to only *o*-phenoxybenzoic acid according to the following:

$$n\text{-}C_4H_9Br \xrightarrow{Li} n\text{-}C_4H_9Li \xrightarrow[2.\ H_3O^+]{1.\ CO_2} n\text{-}C_4H_9CO_2H$$



The extent to which *n*-butyllithium forms and the extent to which it metalates the phenyl ether present depends upon the time of reaction and upon the concentration of the reactants.

In view of the ready formation of *n*-butyllithium in phenyl ether, it appeared altogether reasonable that *n*-butylmagnesium bromide might form in the same solvent. Actually, we have found this to be the case, although the yield of this Grignard reagent is very small. It seems fair to conclude that some of the homologous *n*-amylmagnesium bromide[1] may be formed under corresponding conditions.

EXPERIMENTAL[7]

n-Butyllithium in phenyl ether (*Run 1*). To a stirred mixture of 85.1 g. (0.5 mole) of freshly distilled phenyl ether containing 1.74 g. (0.25 g.-atom) of finely cut lithium wire was added 17.3 g. (0.125 mole) of *n*-butyl bromide over a period of 20 min. Subsequent to the addition the solution became turbid and slight warming was noticed. Color Test I[8] was positive, and Color Test II[9] was negative. The reaction mixture was warmed to 50° and kept at this temperature for 112 hr. Carbonation by means of a Dry Ice–ether slurry and subsequent alkaline extraction gave 5.20 g. (19.7%) of crude *o*-phenoxybenzoic acid. Recrystallizations from ethanol-water, and from petroleum ether (b.p. 60–70°) gave 3.37 g. (12.6%) of pure acid, m.p. and mixed m.p. 111–113°.

n-Butylmagnesium bromide in phenyl ether. To 3.0 g. (0.123 g.-atom) of magnesium turnings and 81.5 g. (0.5 mole) of phenyl ether was added 8.65 g. (0.0625 mole) of *n*-butyl bromide. Inasmuch as no reaction took place, the mixture was stirred for several hours at room temperature with no indication of reaction. A crystal of iodine was added and the mixture allowed to stir overnight at 70°. Color Test I was still negative. The temperature was increased to 120–130° in which range a white precipitate began to form slowly incidental to frothing of the mixture. Color Test I became positive indicating the presence of a Grignard reagent. The mixture was allowed to stir at this temperature for 24 hr., cooled, and then carbonated by pouring into a Dry Ice–ether slurry. Subsequent to hydrolysis and work-up in a customary manner there was obtained valeric acid, which formed a derivative with *p*-toluidine to give 0.42 g. of the *p*-toluidide of valeric acid; m.p. and mixed m.p. 71–72°.

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Derivatives of Some Nitroalkanes

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Simple methods for the preparation of solid derivatives of nitroalkanes are sparse. Usually a nitroalkane is characterized by reduction of the nitro group to a primary amine followed by an acylation or benzoylation of the amine, or alternatively the sodium salt of a nitroalkane is treated with 2,4-dinitrobenzenesulfenyl chloride to form solid α-nitro sulfides.[1–3] Sodium salts of nitroalkanes can also be coupled with aryldiazonium salts to yield solid derivatives.[4]

Primary and secondary nitroalkanes have been shown to undergo the Mannich type condensation with ease and in the case of 2-nitropropane a num-

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(7) Organometallic reactions were carried out under an atmosphere of dry, oxygen free nitrogen. Melting points are uncorrected.

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