Anal. Calcd. for $C_{16}H_{18}N_4S_2$: C, 58.17; H, 5.49; N, 16.96. Found: C, 57.99; H, 5.62; N, 16.70.

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An Improved Procedure for the Dimetalation of Diphenyl Ether

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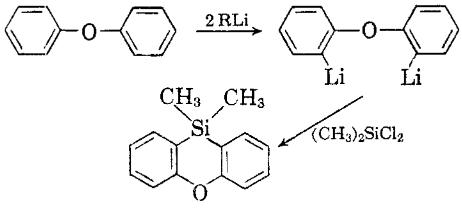
The dimetalation of diphenyl ether has been reported[1] to take place when two equivalents of *n*-butyllithium are refluxed with diphenyl ether for seventy-two hours. The position of dimetalation was established by carbonation of the dilithium intermediate to yield the known acid, 2,2′-dicarboxydiphenyl ether. Further proof was obtained by reaction of the 2,2′-dilithiodiphenyl ether with R_2-SiX_2 reagents to obtain the appropriate cyclic silicon compounds.[1,2]

The long reaction time (seventy-two hours) and the low yield of product (25.1%) prompted the development of some modifications in the dimetalation procedure. The reaction was reinvestigated both in regard to the organometallic reagent and to the solvent system. Derivatization was carried out through the use of dichlorodimethylsilane to obtain the cyclic silicon compound, 10,10-dimethylphenoxasilin.[1]



The results of the investigation are summarized in Table I.

In had been shown previously that, in almost every metalation reaction, the use of tetrahydrofuran gave significantly higher yields of metalated product compared to those obtained in diethyl ether.[3] The present investigation also indicated the much greater activating effect of tetrahydrofuran in metalation reactions. Diphenyl ether was dimetalated quite rapidly by *n*-butyllithium in this solvent, and in a mixed tetrahydrofuran-ether solvent system. The reaction in the mixed solvent system actually gave a greater yield of derivative (50.5%) than when carried out in tetrahydrofuran alone (16.6%). Phenyllithium in the mixed solvent system was also sufficiently reactive to effect dimetalation, but to a lesser extent (23.7%) than *n*-butyllithium. Methyllithium in tetrahydrofuran did not give a derivative indicative of dimetalation.

The use of a mixed solvent system increased the stability of the organolithium reagents. Whereas *n*-butyllithium in tetrahydrofuran alone is very unstable even at room temperature,[4] the use of mixed tetrahydrofuran ether solvent allowed the reaction to be run either at room temperature or at a mild reflux.

The optimum conditions for the dimetalation of diphenyl ether finally developed involved the preparation of *n*-butyllithium (1*N*) in diethyl ether, followed by addition to a tetrahydrofuran solution of diphenyl ether. The final solvent ratio of ether to tetrahydrofuran was about 1.3:1 for a maximum yield at a reasonable reaction time. The reaction mixture can be warmed mildly for five hours before use to obtain a maximum yield (50.5%), or it can be stirred at room temperature for fourteen hours. The latter choice gave a lower yield of derivative (32.0%), but proved convenient because the reaction mixture could be stirred overnight before subsequent reaction. The former choice required closer attention.

The only limiting factor in the dimetalation appears to be a lower yield due to handling difficulties when large quantities of reagents are employed. Notwithstanding, the procedure appears to improve greatly over the seventy-two hours of refluxing used previously to obtain a 25.1% yield of product.

EXPERIMENTAL[5]

Dimetalation of diphenyl ether by n-butyllithium in tetrahydrofuran-ether mixed solvent (1:1) *at room temperature.* To a solution of 25.5 g. (0.15 mole) of diphenyl ether and 250 ml. of tetrahydrofuran was added slowly 0.35 mole of *n*-butyllithium in 290 ml. of ether solution. The reaction flask was cooled at ice-bath temperature throughout the addition, which was completed in 25 min. The ice bath was removed and stirring was continued. The dark green reaction mixture gave a strongly positive Color Test II.[6] Six hours later, Color Test II gave an initial negative test, but a dark reddish brown color developed upon standing. Eight hours later the same results were obtained, and it was concluded that this was a

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(1) K. Oita and H. Gilman, *J. Am. Chem. Soc.*, **79**, 339 (1957).

(2) H. Gilman and D. Miles, *J. Org. Chem.*, **23**, 1363 (1958).

(3) (a) H. Gilman and R. D. Gorsich, *J. Org. Chem.*, **22**, 687 (1957). (b) D. W. Mayo, P. D. Shaw, and M. Rausch, *Chem. and Ind.* (*London*), 1388 (1957). (c) H. Gilman and S. Gray, *J. Org. Chem.*, **23**, 1476 (1958). (d) P. Tomboulian, *J. Org. Chem.*, **24**, 229 (1959).

(4) H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 1165 (1957).

(5) All melting points are uncorrected. Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. Tetrahydrofuran was freed from peroxides and moisture before use by refluxing over sodium, followed by distillation from lithium aluminum hydride.

(6) H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **60**, 1847 (1940).

TABLE I

DIMETALATION OF DIPHENYL ETHER

Organometallic Reagent	Solvent	Solvent Ratio	Reaction Conditions Temp.	Hr.	Yield of Cyclic Derivative, %
n-Butyllithium	THF[a]-ether	1:1	Room temp.	14	32.0
n-Butyllithium	THF-ether	1:1.1	Mild reflux	4	45.5
n-Butyllithium	THF-ether	1:1.3	Mild reflux	5	50.5
n-Butyllithium	THF	—	−25 ± 5 + 0	5 + 12	16.6
Phenyllithium	THF-ether	1:1	Mild reflux	12	23.7
Methyllithium	THF	—	Mild reflux	12	0

[a] THF is tetrahydrofuran.

negative test. Color Test I[7] was strongly positive. The reaction mixture was poured jet-wise through a glass wool plug into a dried, nitrogen swept, addition funnel prior to derivatization.

Derivatization of the 2,2′-dilithiodiphenyl ether was carried out with 19.4 g. (0.015 mole) of dichlorodimethylsilane dissolved in 250 ml. of tetrahydrofuran in essential accordance with the published procedure.[1] The crude 10,10-dimethylphenoxasilin obtained weighed 17.8 g. (52.5%) and melted over the range 60–74°. Two recrystallizations from methanol raised the melting point to 74–79° (lit. m.p.,[1] 78.5–79.0°), 10.8 g. (32.0%). The material was not obtained in an optimum degree of purity, as the relative amounts obtained were of major importance. The melting point of a mixture with an authentic sample was undepressed, and the infrared spectra were superimposable.

The reaction was repeated under identical conditions but using larger quantities (2.5 times greater). The large bulk of the solutions proved difficult to handle and a lower yield of crude derivative was obtained (33.5%).

Dimetalation of diphenyl ether by n-butyllithium in tetrahydrofuran-ether mixed solvent at mild reflux. (*A*). *1:1.1 Tetrahydrofuran-ether ratio.* A 440-ml. ether solution containing 0.575 mole of *n*-butyllithium was added rapidly to a solution of 42.5 g. (0.25 mole) of diphenyl ether and 350 ml. of tetrahydrofuran cooled to ice-bath temperature. The ice bath was removed, and the reaction mixture was warmed to a mild reflux temperature. Color Test II remained positive for 3 hr., but became negative after 4 hr. Color Test I was positive.

Derivatization was effected with 32.2 g. (0.25 mole) of dichlorodimethylsilane dissolved in 350 ml. of tetrahydrofuran as described in the previous experiment. Recrystallization of the crude solid from methanol gave 25.8 g. (45.5%) of 10,10-dimethylphenoxasilin, m.p. 75–79°.

(*B*). *1:1.3 Tetrahydrofuran-ether ratio.* The above procedure was followed in the reaction of 46.8 g. (0.275 mole) of diphenyl ether dissolved in 400 ml. of tetrahydrofuran with 0.605 mole of *n*-butyllithium in 590 ml. of ether solution. A total of 5 hr. of mild reflux was necessary before Color Test II became negative. Derivatization with dichlorodimethylsilane gave 28.5 g. (50.5%) of 10,10-dimethylphenoxasilin, m.p. 74–79°.

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(7) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

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gem-Dinitro Esters. III. Esters of 2,2-Dinitropropanol[1]

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A number of esters of 2,2-dinitropropanol[2] were prepared and some of their physical properties measured during the screening of energy contributing compounds for plasticizing action in plastic bonded explosives (PBX). The use of energy contributing plastics and plasticizers would be expected to enhance the performance of the plastic bonded explosives described by James, Smith, and coworkers.[3]

Most of the esterifications were accomplished under mild conditions employing trifluoroacetic anhydride[4] or polyphosphoric acid[5] as condensing agent. In general, the purification of the esters was simpler when the former agent was used. In cases where both methods were used, the one giving the higher yield appears in the accompanying table. Table I also lists the physical properties measured. When tested, all the compounds in Table I appeared to be less sensitive than 2,4,6-trinitrotoluene to impact.

The carbonyl absorptions in the infrared[6] were shifted to shorter wave lengths compared to unsubstituted esters and occurred between 5.64 and 5.67 μ for all of the esters of the carboxylic acids except the formate and 2-methylacrylate (5.72 μ),

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(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) OSRD Report No. 2016, November 15, 1943.

(3) E. James, L. C. Smith, W. T. Barry, K. B. Fess, W. A. Lynch, C. L. Miller, J. B. Panowski, M. Schwartz, W. H. Stein, M. J. Urizar, D. W. Niemand, E. E. Shaw, and R. F. Warner, *U. S. At. Energy Comm.* LA-1448 (1952); *Chem. Abstr.*, 54, 21762 (1960).

(4) E. J. Bourne, M. Stacey, J. C. Tatlow, and J. M. Tedder, *J. Chem. Soc.*, 2976 (1949).

(5) The commercial product named "Polyphosphoric Acid" manufactured by the Victor Chemical Co. was used in this work.

(6) Infrared absorption spectra were determined with a Model 21 Perkin-Elmer instrument with matched 0.1-mm. sodium chloride cells and chloroform as solvent.