The Use of Organodilithium Compounds for the Synthesis of 1,1-Dimethylsilacyclopentane and 1,1-Dimethylsilacyclohexane[1]

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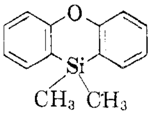
Organodilithium compounds have been successfully employed for the preparation of sila-heterocyclic compounds,[2] such as 10,10-dimethylphenoxasilin (I).[3] However, organodilithium compounds have not been extensively employed for the synthesis of compounds such as II and III. Tamborski and Rosenberg[5] have reported that the reaction of 1,5-dilithiopentane and dimethyldichlorosilane failed to yield compound II. Wittenberg and Gilman,[4] however, report that 1,1-diphenylsilacyclopentane may be prepared in 46% yield from 1,4-dilithiobutane and diphenyldichlorosilane.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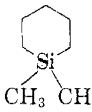
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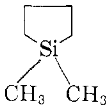
III

Compounds II and III have been previously prepared utilizing a two-step synthesis.[5] The ring closure reaction was accomplished by reaction of the di-Grignard reagent with silicon tetrachloride. The second step of the synthesis was accomplished by reaction of the resulting dichlorosilacycloalkane with either methyl Grignard reagent[5] or methyllithium.[6]

In this investigation, it has been observed that a modification of the reaction conditions of Tamborski and Rosenberg[6] will allow the direct preparation of II and III from the appropriate dilithioalkane and dimethyldichlorosilane.

In order to obtain the best yield of III, a mixture of 1,4-dibromobutane and dimethyldichlorosilane was added to a chilled mixture of lithium shot[7] using an ether solvent. The reaction was exothermic and a Dry Ice–acetone bath was necessary for cooling. The rate of addition of the mixture did not appear to be of importance if the reaction temperature was kept below 20°. Using this procedure, the yields of III varied from 54 to 76%. Dilution reduced the yield of III to 40%. When the dilithium reagent was prepared prior to the addition of dimethyldichlorosilane, the yield of III was 42%.

Compound II could be obtained in yields of only 27 to 32% using this procedure. In a run when the dilithium reagent was prepared prior to the addition of dimethyldichlorosilane, no silacyclohexane was obtained. This latter observation is in agreement with the report of Tamborski and Rosenberg.[6]

No cyclic silanes were obtained when 1,4-dichlorobutane, 1,4-dichloro-2-butene or 1,3-dibromopropane were used in this reaction.

EXPERIMENTAL[8]

1,1-Dimethylsilacyclopentane (III). In a 1-l. flask, equipped for a nitrogen atmosphere and fitted with a mechanical stirrer dropping funnel, and reflux condenser with a thermometer insert, were placed 300 ml. of dry ether and 11.2 g. (1.60 moles) of lithium shot.[4] The reaction flask was then cooled to 10° with a Dry Ice–acetone bath. To this mixture was then added dropwise (CAUTION) a mixture of 51.6 g. (0.40 mole) of dimethyldichlorosilane and 86.4 g. (0.40 mole) of 1,4-dibromobutane. Throughout the addition period (*ca.* 1 hr.) care was taken to maintain the temperature of the reactants below 20°. After the addition had been completed, the mixture was heated under reflux for 1 hr. then filtered to remove the lithium halide. The filter cake was washed with three 100-ml. portions of ether. The ethereal solution was concentrated to *ca.* 100 ml., then filtered to remove the lithium halide precipitated during the concentration. Distillation resulted in 29.1 g. (65%) of 1,1-dimethylsilacyclopentane (III), b.p. 103–105°, n_D^{23} 1.4340 (lit.[5] b.p. 107°, n_D^{25} 1.4334). Yields varied from 54 to 76%.

In one run when 500 ml. of ether was used with 0.2 mole of reactants, only a 40% yield of dimethylsilacyclopentane was obtained.

In another run when the 1,4-dilithiobutane (0.20 mole) was prepared prior to the reaction with dimethyldichlorosilane, a 42% yield of the dimethylsilacyclopentane was obtained.

When 1,4-dichlorobutane was used in place of 1,4-dibromobutane no precipitation of lithium halide was observed and no dimethylsilacyclopentane was obtained.

1,1-Dimethylsilacyclohexane (II). Using the procedure described for the preparation of the silacyclopentane, 5.6 g. (0.80 mole) of lithium shot,[7] 25.8 g. (0.20 mole) of dimethyldichlorosilane, and 46.0 g. (0.20 mole) of 1,5-dibromopentane yielded 8.5 g. (33%) of 1,1-dimethylsilacyclohexane (II), b.p. 129–131°, n_D^{23} 1.4421 (lit.[5] b.p. 133°, n_D^{25} 1.4380). In another run using the same procedure, the yield of II was 27%.

In another reaction when 0.1 mole of 1,5-dilithiopentane was prepared prior to addition of dimethyldichlorosilane, only nondistillable residue was obtained.

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(1) This work was supported by a Frederick Gardner Cottrell grant from Research Corp.

(2) (a) H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **77**, 6380 (1955); (b) K. Oita and H. Gilman, *J. Org. Chem.*, **22**, 336 (1957); (c) C. H. S. Hitchcock, F. G. Mann, and A. Vanterpool, *J. Chem. Soc.*, 4537 (1957); (d) K. Oita and H. Gilman, *J. Am. Chem. Soc.*, **79**, 339 (1957); (e) H. Gilman and D. Miles, *J. Org. Chem.*, **23**, 1363 (1958); (f) H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **80**, 1883 (1958).

(3) Ref. 2(c) and 2(d).

(4) D. Wittenberg and H. Gilman, *J. Am. Chem. Soc.*, **80**, 2677 (1958).

(5) R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954).

(6) C. Tamborski and H. Rosenberg, *J. Org. Chem.*, **25**, 246 (1960).

(7) R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 1739 (1953).

(8) All boiling points are uncorrected. Distillations were accomplished using a 2-meter modified Podbielniak column (*cf.* J. Cason and H. Rapoport, *Laboratory Text in Organic Chemistry*, Prentice-Hall, Inc., New York, 1950, p. 237) and were run at atmospheric pressure.

Reactions with 1,4-dichloro-2-butene (0.10 molar reaction) and with 1,3-dibromopropane (0.20 molar reaction) using the same solvent ratios and procedures as described for compound III, resulted in nondistillable residues.

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Amine Oxidations with Iodine Pentafluoride. Preparation of Azoisobutane[1]

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Several organic amines, and some related organic compounds, have been exposed to the mild fluorinating agent, iodine pentafluoride,[2] in methylene chloride or methylene chloride–pyridine solutions. The results of some of these experiments are summarized in Table I. Although most organic amines were observed to react vigorously when mixed with iodine pentafluoride, a controllable interaction occurred in the presence of the inert solvent. In the experiments reported in the table, hydrolysis of the reaction mixture was carried out before isolation of any products was attempted; hence, some of the materials isolated were formed by hydrolysis of uncharacterized intermediates.

The first five examples in the table illustrate the dehydrogenation of a primary amine containing an α-methylene group. With pyridine present in the reaction mixture it was possible to isolate the corresponding nitrile in 50–90% yield. Since the aldehyde accompanying the nitrile probably arises from hydrolysis of an imine (the product of

$$\text{R—CH}_2\text{NH}_2 \xrightarrow[\text{(2) H}_2\text{O}]{\text{(1) IF}_5} \text{R—CN} + \text{RCHO}$$

incomplete dehydrogenation), conditions better for this dehydrogenation than those given in the table may exist.[3]

t-Butylamine was oxidized readily to 2,2′-dimethyl-2,2′-azopropane (azoisobutane). This method of preparation of this interesting and useful azo compound appears to be quite superior to that reported.[4] However, vapor phase chromatography of the azoisobutane produced in the iodine pentafluoride oxidation indicated a very small amount of impurity that was not removed readily by washing and distillation. Chromatographic purification of samples might be required to obtain uncontaminated material.

Hydrazobenzene was oxidized readily to azobenzene. There was no sign of further reaction iodine pentafluoride and azobenzene; solutions of azobenzene in pure iodine pentafluoride were warmed to 100°, and the azobenzene was recovered unchanged upon hydrolysis of the iodine pentafluoride.

Although oxidation of dibenzylamine and tribenzylamine proceeded smoothly to produce benzaldehyde, oxidation of other secondary and tertiary amines, of primary amines containing an α-substituent, and of aromatic amines led mostly to uncharacterized, tarry products.

Oximes, when added to a methylene chloride solution of iodine pentafluoride, underwent a Beckmann rearrangement. The last three examples in the table illustrate this. Hydrolysis of unchanged oxime during the processing of the reaction mixture appeared to be the major side reaction, although some of the acetanilide produced in the acetophenone oxime rearrangement underwent aromatic iodination.

EXPERIMENTAL

Melting points and boiling points are uncorrected. Iodine pentafluoride was obtained from the Matheson Co.; it was pumped *in vacuo* from the cylinder, trapped in a Kel-F test tube at −78°, and allowed to melt in a stream of dry nitrogen. The test tube then was detached from the vacuum line and the iodine pentafluoride was withdrawn and measured in a glass pipet.

Reaction of iodine pentafluoride and amines. Not all of the amine reactions mentioned in the table are detailed here, but the methods and results are illustrated amply.

(a) *Benzylamine.* A solution of 3.0 ml. (0.043 mole) of iodine pentafluoride in 120 ml. of methylene chloride was cooled to 3° and 4.3 g. (0.040 mole) of benzylamine in 30 ml. of methylene chloride was added dropwise over 30 min. The solution was stirred at 15° for 2 hr. Ice water then was added and the methylene chloride was separated and washed with dilute hydrochloric acid, water, and dilute sodium thiosulfate solution. Evaporation of the methylene chloride left 1.35 g. of residue. The infrared spectrum of this oil indicated that it was a benzonitrile-benzaldehyde mixture. The sample was chromatographed on Perkin-Elmer vapor phase chromatogram Column A at 150°, utilizing acetophenone as an internal standard. In this way it was determined that the residue consisted of benzaldehyde, 0.84 g. (20%), and benzonitrile, 0.35 g. (9%). The retention time of the benzaldehyde and of the benzonitrile was the same as that of the authentic material used in obtaining the calibration curves.

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(1) This research was carried out under Army Ordnance Contract DA-01-021-ORD-5135.

(2) M. C. Sneed, J. L. Maynard, and R. C. Brasted, *Comprehensive Inorganic Chemistry*, Vol. III, *The Halogens*, D. Van Nostrand Co., Inc., New York, N. Y., 1954, pp. 210–13; General Chemical Division, Allied Chemical and Dye Corporation, Technical Bulletin TA-8532-2, "Chlorine Trifluoride and Other Halogen Fluorides."

(3) As a referee has pointed out, there is an analogy between these dehydrogenations and those reported in the Hofmann rearrangement for certain amines of intermediate size [see E. S. Wallis and J. F. Lane, *Org. Reactions*, **3**, 267 (1946)]. One could postulate the formation of *N*-fluoroamine intermediates in these oxidations, as *N*-bromoamines were considered to be intermediates in the hypobromite oxidations (R. C. Fuson, *Advanced Organic Chemistry*, John Wiley and Sons, New York, 1950, p. 538), but no evidence was found for such species. The basic fractions of these reactions, and of those mentioned later, were not examined for coupling products.

(4) E. Farenhorst and E. C. Kooyman, *Rec. trav. chim.*, **72**, 993 (1953).