

COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME 26

ANNÉE 1980

**A Study On The Electrophilic Amination of Phenyllithium
And Phenylmagnesium Bromide**

by

ENDER ERDIK

1†

Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Université d'Ankara

Comité de Rédaction de la Série B

A. Olcay, C. Tüzün, Y. Sarıkaya

Secrétaire de Publication

Ö. Çakar

La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara" est un organe de publication englobant toutes les disciplines scientifiques représentées à la Faculté.

La Revue, jusqu'à 1975 à l'exception des tomes I, II, III, était composée de trois séries:

Série A: Mathématiques, Physique et Astronomie

Série B: Chimie

Série C: Sciences naturelles

A partir de 1975 la Revue comprend sept séries:

Série A₁: Mathématiques

Série A₂: Physique

Série A₃: Astronomie

Série B : Chimie

Série C₁: Géologie

Série C₂: Botanique

Série C₃: Zoologie

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté. Elle accepte cependant, dans la mesure de la place disponible, les communications des auteurs étrangers. Les langues allemande, anglaise et française sont admises indifféremment. Les articles devront être accompagnés d'un bref sommaire en langue turque.

Adres: Fen Fakültesi Tebliğler Dergisi Fen Fakültesi, Ankara, Turquie.

A Study On The Electrophilic Amination of Phenyllithium And Phenylmagnesium Bromide

ENDER ERDİK*

Institute of General Chemistry, Faculty of Science, Ankara University, Ankara,
Turkey

(Received on 11 October 1980 and accepted on 2 November 1980)

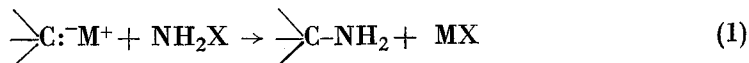
The electrophilic amination of phenyllithium and phenyl Grignard reagents with *O*-methylhydroxylamine (I) has been reinvestigated. The effects of the solvent, the reaction temperature and the PhLi / I stoichiometry on the amination yield have been discussed and a mechanism involving the formation of mono- and dilithio derivatives of I as intermediates, has been proposed. The conditions for the amination of an organolithium or Grignard reagent are optimized to be as follows: An ethereal solution of I is added in a 3:1 organolithium / I mole ratio to an ethereal solution of organolithium at -15° . The use of *O*-mesitylenesulfonylhydroxylamine as an amino transfer reagent and the examination of organocopper reagents to aminate with I are found to decrease the amination yield. This survey has revealed that I remains as a convenient reagent for the amination of organolithium and Grignard reagents.

INTRODUCTION

The introduction of amino functionality into the organic molecules, is generally accomplished¹ by using the nitrogen containing nucleophiles. Hoffman alkylation, Gabriel synthesis and the formation and subsequent reduction of Schiff bases are known as classical examples. However, certain reagents containing amino groups react with the nucleophiles such as carbanions, amines, sulfides, sulfoxides and phosphines to give the corresponding aminated products². Amines represented by the general structure NH_2X (where X is a leaving group) are good amino-transfer reagents. Such compounds include hydroxylamine-*O*-sulfonic acid ($\text{X}=\text{OSO}_2\text{OH}$)³, monochloramine ($\text{X}=\text{Cl}$)⁴, *O*-alkyl-

* Mailing address: A.Ü. Fen Fakültesi, Ankara, Turkey.

and O-arylhydroxyl amines ($X=OR$ or OAr)⁵ and O-acyl- and O-arensulfonylhydroxylamines ($X=OCOAr$ or OSO_2Ar)². Although there are numerous examples for the amination of nucleophiles with these reagents², only a few reports have been published about the amination of carbanions, especially organometallic compounds (1). Scheverdina and Kotscheskow published^{6a} the synthesis of some alkyl and arylamines by the amination of

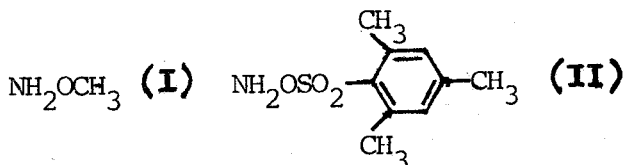
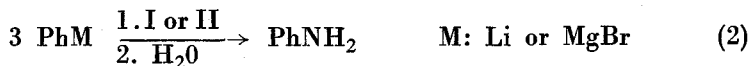


of corresponding organolithium and Grignard reagents with O-methylhydroxylamine. Brown and Jones^{6b} reported the amination of alkyl Grignard reagents with O-methylhydroxylamine and by this method, a number of heterocyclic compounds were aminated⁷ via their lithio derivatives. Monochloramine was also used for the amination of Grignard reagents⁸. Brown, et al.⁹ reported that organoboranes reacted with monochloramine and hydroxylamine-O-sulfonic acid to afford the primary amines; however Tamura, et al.¹⁰ found O-mesitylene sulfonylhydroxylamine to be superior as an electrophilic amino transfer reagent for organoboranes. N,N-Dialkyl-O-mesitylenesulfonylhydroxylamine was used by Boche, et al.¹¹ to dialkylaminate various organolithium compounds. Toguri, et al. found¹² O-methylhydroxylamine to be the best for the amination of O-lithiated carboxylic acids. Very recently, Loudon and Miller¹³ have published a detailed paper reporting that 2-substituted malonate esters aminate with O-(2,4 dinitrophenyl) hydroxylamine and 2-aminomalonates thus produced are converted to the amino acids by hydrolysis and decarboxylation.

The objective of the study described in this paper was to investigate new reagents and routes for the electrophilic amination of organolithium and Grignard reagents. Here, the results of the observation on the influence of the reaction conditions on the amination reactions of phenyllithium, phenylmagnesium bormide and their copper (I) ate complexes, are reported.

RESULTS AND DISCUSSION

The reaction of phenyllithium and phenyl Grignard reagent with O-methylhydroxylamine (I)



The reaction 2 was investigated to see the effects of the stoichiometry of the amino transfer reagent, the reaction temperature and the solvent on the amination yield and the outcome of the reaction. The reactions throughout this work were carried out in small scale and the products were identified and the yields were determined by glpc.

It is evident that 3 mols of PhM must be used in the reaction with 1 mole of I, i.e. 2 mols for the deprotonation of amino hydrogens and 1 mole for the electrophilic substitution. For the amination of alkyl Grignard reagents with I, alkyl Grignard / I mole ratio was reported^{6b} to be 2:1; but, the amination of the lithio derivatives of some heterocyclic compounds were reported⁷ to occur via a 3:1 organolithium / I stoichiometry. On the other hand, there are numerous reports¹⁴ indicating that the Grignard reagents abstract one hydrogen of amino groups at room temperature or at lower temperatures. Lithium reagents may well react¹⁵ with both protons of the primary amines depending upon the reaction conditions. These results about the protonation of the amino group might seem to be in accordance with those found in the amination studies. However, from the results in this work, it is clear that the maximum yield of aniline is obtained when the PhLi (or PhMgBr) / I mole ratio is 3:1. By lowering this ratio from 3:1 to 2:1 in a reaction carried out at the optimum conditions (see below), the yield of aniline drops from 50-53 % to 30-38 %.

In order to overcome the difficulty of maintaining a 3:1 organolithium(or Grignard reagent)/I stoichiometry for the amination and thus to save expensive or hardly prepared organolithium or Grignard reagents, a number of ways were tried. Firstly, it was obtained that the amination of PhI with I even in a reaction carried out at -78° requires again 3:1 PhLi/I ratio and results in a yield which is the same with that found at -15° . This suggests that the abstraction of the two protons even occurs at -78° and gives an evidence for that the amination goes to completion even at -78° . Therefore, treating I first with an expendable lithium reagent in a 2:1 RLi / I ratio at a low temperature and then with the lithium reagent to be aminated, as pointed out by Wakefield¹⁶ would not solve the above mentioned problem. It was indeed found that treating I first with n-Buli in a 2:1 n-Buli/I ratio and then with PhLi (or PhMgBr), results in lower yields of aniline, i.e. 6 % and 15 % with PhLi and PhMgBr, respectively. In order to examine the deprotonation of I with a base which does not normally act as a nucleophile, I was allowed to react with sodium. In a reaction with a 1:1 Na / I mole ratio in Et₂O, sodium was completely consumed by a gas evolution producing sodium methoxide. Addition of PhLi to the resulting suspension was found to give 15-20 % yield of aniline. Moreover in the IR analysis of the precipitated MeONa, the absorption band for the N-H group was detected.

From the results of the study for the deprotonation of I by a base other than the lithium reagent to be aminated, it is evident that I is decomposed in the presence of bases. While carrying out these experiments, Miller and Loudon's paper¹³ describing the base mediated decomposition of NH₂X reagents appeared and therefore no further experiments were done. The complete failure of the attempted deprotonation of I prior to the amination would seem to indicate that the mono and dimetallated derivatives of I are not stable and must be formed in situ in the course of the amination.

The reaction 2 was examined at various temperatures and in different solvents. The highest yield of of aniline is obtained by carrying out the reaction at either -15° or 0° ; lowering the tempe-

perature to -78° does not make a difference in the amination yield and outcome of the reaction. A reaction at the room temperature results in a decreased yield. The use of THF or benzene as a solvent instead of Et_2O does not increase the yield appreciably. TMEDA used as a solvent or in an equivalent amount to PhLi produces a substantial lowering of the aniline yield. An explanation for this can be that the presence of a strong base would increase the above mentioned decomposition of I. As the yield of the aminated product shows the competition between amination and decomposition of I, the inverse addition, i.e. the addition of PhLi to a Et_2O solution of I and the concentration of the reaction solution are found not to affect the yield.

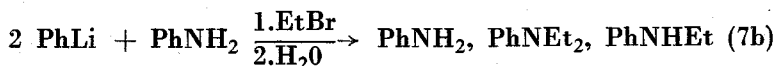
The use of a catalyst, such as anhydrous AlCl_3 , to enhance the electrophilicity of I, as reported¹⁷ for the amination of arenes with I, can not be tried since PhLi is known¹⁸ to react with AlCl_3 .

The conditions for the reaction 2 are optimized as follows: A solution of I in Et_2O is added to PhLi (or PhMgBr) in Et_2O or THF solution in a 3:1 PhLi (or PhMgBr) / I mol ratio at -15° or 0° . After the addition, the reaction mixture is kept in the cooling bath for half an hour and allowed to come to room temperature and kept at that temperature for a further half an hour.

No attempt was made to set up the material balance in the reaction 2 although c.a 40 % of I could not be accounted for the amination. However, a GC-MS analysis of the reaction products after hydrolytic work up showed the presence of diaminobenzenes, bromoanilines, aminobiphenyls, bromobiphenyls, aminobromobiphenyls, terphenyls and bromoterphenyls.

The proposed mechanism for the reaction of phenyllithium with O-methylhydroxylamine (I)

Likely mechanisms for the amination of PhLi (or PhMgBr) with the amino transfer reagent I are shown in the reactions (3-5):



If the anions III and VI are produced by the substitution of PhLi with the previously protonated I, i.e. MeONLi₂ and MeONHLi (the mechanism 3) and not by the deprotonation of the product PhNH₂ with unsubstituted PhLi (the mechanism 5), then the yield of PhNEt₂ in Expts. 7a, b. would not be the same with that found in Expts. 6a, b. Trapping experiments gave the following results: The yields of PhNH₂, PhNHET and PhNEt₂ at -15° were found to be 40 %, 5 % and 5 % respectively in Expt. 6 a and 50 %, 1 % and 7 % respectively in Expt. 6b. Expt. 7a, carried out at the room temperature resulted in a 18 % yield of PhNHET and less than 1 % PhNEt₂ and at -15°, 22 % yield of PhNHET and 2 % PhNEt₂; Expt. 7 b run at the room temperature produced a 15 % yield of PhNHET and less than 1 % yield of PhNEt₂ (by metallation at refluxing temperature, the yield of PhNHET dropped to 2 %). The result that trapping by Expts. 6 a,b gives a higher yield of PhNEt₂ but a lower yield of PhNHET than that obtained in Expts. 7 a,b indicated that PhLi abstracts one proton of PhNH₂, but two protons of I at the above mentioned reaction conditions. Certainly, this fact requires the formation of the anion III by the substitution of PhLi with the preliminary intermediate MeONLi₂ and provides evidence concerning the mechanism 4 or at least suggests that the mechanism 5 is not involved.

The use of O-mesitylenesulfonylhydroxylamine (II) to aminate phenyllithium or phenylmagnesium bromide

The O-alkylhydroxylamines other than I and O-arylhydroxylamines and hydroxylamine-O-sulfonic acid were not tried in this work, as they were reported¹² to be less efficient amino transfer reagents than I. O-Mesitylenesulfonylhydroxylamine (II) was tried to aminate PhLi and PhMgBr. However, the difficulty of preparing² IV in strictly anhydrous conditions might be a problem which causes a decreased yield of amination. Indeed, the yield of PhNH₂ from the amination of PhLi or PhMgBr with I did not exceed 30 % in spite of all efforts; the normal addi-

tion gave a 18-23 % yield and the inverse addition 20-32 % yield. On the other hand, *N,N*-dialkyl-*o*-mesitylenesulfonhydroxylamine was reported¹³ to dialkylaminate various organometallic reagents in good yields. These results suggest that the presence of amino hydrogens leads to base mediated decomposition of II producing a lowered amination yield. Support for this conclusion comes from the fact that the amination with *o*-2,4-dinitrophenylhydroxylamine, was reported to be a synthetically useful reaction only in the case of enolate anions of basicity comparable to malonates but drop off considerably as the enolate becomes more basic. Therefore, the low amination yield of PhLi or PhMgBr with II is in part the result of the rather high basicity of these organometallics. But in the case of amination with I, the deprotonation leading to the composition of I is expected to be less efficient than that with II as the methoxy group is a poorer leaving group making the protons of I less acidic than that of II.

*Amination of various phenyl copper reagents with *o*-methylhydroxylamine (I)*

Organocopper substitution reactions with carbon electrophiles have ever been applied successfully for C-C bond formation¹⁹. In this work various classes of phenyl copper (I) species have been investigated as reagents in substitution reactions with the amino transfer reagent I.

Among them Ph(Me)CuMgBr²⁰ was reported to be a reagent for selectively transferring the Grignard reagent derived phenyl group in high yield although Ph₂LiCu²¹ has the disadvantage that one equivalent of the phenyl group is inevitably wasted. Organocopper reagents also show low basicity toward protons, which might be a factor decreasing the decomposition of I. However, phenylcopper²¹, PhCu, diphenyllithium cuprate²², Ph₂LiCu and phenyl (methyl) copper (I) magnesium bromide²⁰ Ph (Me) CuMgBr, have all failed to give even a comparable amination yield with that obtained from the amination of PhLi or PhMgBr.

Conclusions

This survey has revealed that I is a convenient amino transfer reagent for the electrophilic amination of organolithium and Grig-

nard reagents. The use of THF or benzene instead of Et₂O as a solvent does not increase the yield appreciably, however TMEDA leads to decomposition of I. The stoichiometry of the reaction requires a 3:1 organolithium: I mole ratio and attempts to deprotonate I by consuming a base other than the excess organolithium have been fruitless. A possible mechanism involving the lithiated derivatives of I can be formulated for the amination of an organolithium reagents with I, The use of various classes of organocopper reagents to aminate with I and the use of O-mesitylenesulfonyldroxylamine as an amino transfer reagent are found to decrease the amination yield.

EXPERIMENTAL SECTION

General

All reactions involving organometallic compounds were carried out under nitrogen atmosphere using standard techniques²³. Melting points were determined with a capillary melting point apparatus. IR spectra were taken on a PE 377 spectrophotometer. NMR spectra were run on a Varian A-60 instrument. Analytical glpc analysis were performed on a PE Model F11 gas chromatograph equipped with a flame ionisation detector and an electronic integrator using a Carbowax 20M-KOH on Chromosorb W column. Products were identified by comparison of their retention times with those of authentic samples and the yields were calculated with the internal standard technique.

Diethylether was distilled from a deep red and tetrahydrofuran from a deep purple solution of disodium benzophenone dianion under nitrogen atmosphere. N,N,N',N'-tetramethylenediamine was distilled over sodium at reduced pressure. Fisher "Grignard Quality" magnesium turnings was used. Lithium dispersion in mineral oil was purchased from BDH. Bromobenzene was dried over anhydrous calcium chloride and fractionally distilled. Copper (I) iodide²⁴ and copper (I) bromide²⁵ were purified according to described procedures. Phenylithium and phenylmagnesium bromide were prepared by conventional methods found elsewhere. Phenylithium was standardized by Gilman double

titration procedure²⁶ and phenylmagnesium bromide by a modified Watson and Eatham method²⁷. Phenylcopper²¹, diphenyllithium cuprate²² and phenyl(methyl) copper (I) magnesium²⁰ bromide were prepared according to the published procedures and used immediately. O-Methylhydroxylamine was prepared by the method of Hjed's and the base was obtained by the distillation of the hydrochloride with a saturated NaOH solution and by passing the vapors through a column packed with NaOH pellets, bp 48-50°(lit.^{5d}49°). O-Mesitylenesulfonylhydroxylamine was prepared by the method of Tamura, et al.² and the mp of the product was found 68-70° in all preparations and not the same with that reported mp. 93-94°; however it was also reported to be 69-70° by Ning²⁸.

General procedure for the amination reactions

All the amination reactions were carried out by using similar procedures described here for the amination of phenyllithium with O-methylhydroxylamine (I). To a flame dried small reaction flask capped with a no air stopper and containing a stirring bar was added phenyllithium in diethyl ether solution (3 mmol) with a hypodermic syringe. The flask was cooled to -15° in an ice-salt bath under a positive nitrogen pressure. A diethylether solution of I (1 mmol) was added dropwise with a syringe. The solution turned to red-brown with a visible evidence of gas evolution formation of a precipitate. The reaction was kept at -15° for half an hour, then allowed to come to room temperature and kept at that temperature for a further half an hour. The products were hydrolyzed with an ammoniacal saturated ammonium chloride solution, extracted with ether, the ether layer was dried and concentrated. The product mixtures were analyzed by glpc using unexceptional internal standard techniques.

Trapping of the mono and dilithio salts of aniline in the reaction of PhLi with I was performed at -15° in two different ways in the inert conditions described above. In a first way, an ethereal solution of I (1 mmol) was added to an ethereal phenyllithium solution containing ethyl bromide (10 mmol); in the second way, I was added to phenyllithium and after the visible gas evolution

had ceased, ethyl bromide was added. The reaction mixtures were kept at -15° for half an hour and a further half an hour at the room temperature. The products were analyzed by glpc after the hydrolytic work up as written above.

Acknowledgement: Financial support for this work from the Scientific and Technical and Research Council of Turkey (Grant no. TBAG- 395) is gratefully acknowledged.

CAS Registry Numbers: Phenyllithium, 591-51-5; phenylmagnesium bromide, 100-58-3; phenylcopper, 3220-19-3; diphenyllithium cuprate, 23402-69-9; phenyl (methyl) copper (I) bromide, 59532-63-7; O-methylhydroxylamine, 67-62-9; O-mesitylenesulfonylhydroxylamine, 36016-40-7; aniline, 62-53-3.

REFERENCES

- 1- C.A. Buehler and D.E. Pearson, "Survey of Organic Synthesis", Wiley, 1970, p. 443.
- 2- (a) Y. Tamura, J. Minamikawa and M.J. Ikeda, *Synthesis*, 1 (1977); (b) Y. Tamura, et al., *J. Org. Chem.*, **38**, 1239 (1973).
- 3- M.W. Rathke and A.A. Millard, *Org. Synth.*, **58**, 32 (1978).
- 4- G.A. Jaffari and A.J. Nunn, *J. Chem. Soc. C*, 823 (1971);
- 5- O-Alkylhydroxylamines: (a) G. Palazzio, et al., *Gazz. Uçim. Ital.*, **84**, 915 (1954); (b) W. Theilacker and K. Ebke, *Angew. Chem.*, **68**, 303 (1956); (c) A. Chimiak and T. Kolasa, *Bull. Acad. Polonaise Sci.*, **22**, 195 (1974); (d) W. Traube, et al., *Ber.*, **53**, 1477 (1920). O-Methylhydroxylamine: (e) H. Hjeds, *Acta Chem. Scand.*, **19**, 1764 (1965). O-Arylhydroxylamines: (f) T. Sheradsky, et al., *Tetrahedron*, **28**, 3833 (1972), (g) A.O. Ilvespaa and A. Marxer, *Helv. Chim. Acta*, **46**, 2009 (1963). O-Phenyldroxyamine: (h) C.L. Baumgardner and R.L. Lilly, *Chem. Ind.*, 559 (1962).
- 6- (a) N.I. Schewerdina and K.A. Kotscheschkow, *Chem. Zentr.*, 1940 I, 360; 1942 I, 1872; (b) R. Brown and W.E. Jones, *J. Chem. Soc.*, 781 (1946).
- 7- (a) H. Gilman and C. Stuckwisch, *J. Am. Chem. Soc.*, **65**, 1461 (1943); (b) H. Gilman and D. Swayanpati, *ibid.*, **79**, 208 (1957); (c) E. Acton and R. Silverstein, *J. Org. Chem.*, **24**, 1487 (1959).
- 8- G.H. Coleman et al., *J. Am. Chem. Soc.*, **63**, 1692 (1941).
- 9- (a) H.C. Brown, et al., *J. Am. Chem. Soc.*, **86**, 3565 (1964); (b) M.W. Rathke, *ibid.*, **88**, 2870 (1966).
- 10- Y. Tamura, et al., *Synthesis*, 196 (1974).
- 11- G. Boche, et al., *Angew. Chem. Int. Ed. Engl.*, **17**, 687 (1978).
- 12- T. Oguri, et al., *Chem. Pharm. Bull.*, **23**, 167 (1975).

- 13- A.S. Radhakrishna, G.M. Loudon and M.J. Miller, *J. Org. Chem.*, **44**, 4836 (1979).
- 14- M.S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances", Prentice Hall, 1954, p. 1166.
- 15- B.J. Wakefield, "The Chemistry of Organolithium Compounds", Pergamon Press, Oxford, 1974, s. 161.
- 16- B.J. Wakefield, *loc. cit.*, p. 215.
- 17- P. Kovacic and R.P. Bennett, *J. Am. Chem. Soc.*, **83**, 221 (1961).
- 18- B.J. Wakefield, *loc. cit.*, p. 257.
- 19- (a) G.H. Posner, *Org. React.*, **22**, 253 (1975); (b) J.F. Normant, *J. Organometal. Chem. Libr.*, **1**, 219 (1976).
- 20 (a) D.E. Bergbreiter and G.M. Whitesides, *J. Org. Chem.*, **40**, 779 (1975); (b) D.E. Bergbreiter and J.M. Killough, *ibid.*, **41**, 3750 (1976).
- 21- A. Camus and N. Marsich, *J. Organometal. Chem.*, **14**, 441 (1968).
- 22- (a) G.H. Posner and K.A. Babiak, *J. Organometal. Chem.*, **177**, 299 (1979); (b) C.R. Johnson and G.A. Dutra, *J. Am. Chem. Soc.*, **95**, 7777 (1973); (c) G.M. Whitesides, et al., *ibid.*, **91**, 4871 (1969).
- 23- (a) D.F. Shriver, "The Manipulation of Air-Sensitive Compounds". McGraw-Hill, 1969. Chap. 7.
- 24- R.N. Keller and H.D. Wycoff, *Inorg. Synth.*, **2**, 1 (1946).
- 25- G. Kaufmann and L.A. Teter, *ibid.*, **7**, 9 (1963).
26. (a) G.M. Whitesides, et al., *J. Am. Chem. Soc.*, **93**, 1379 (1971); (b) W.G. Kofron and L.M. Baclowski, *J. Org. Chem.*, **41**, 1879 (1976).
- 27- S.C. Watson, J.E. Eastham, *J. Organometal. Chem.*, **2**, 165 (1967).
- 28- R.Y. Ning, *Chem. Eng. News*, **51**, (Dec. 17), p. 37 (1973).

ÖZET

Fenillityum'un ve fenilmağnezyum bromür'ün O-metilhidroksilamin (I) ile elektrofilik aminasyonu araştırılmıştır. Aminasyon verimi üzerinde çözücünün, reaksiyon sıcaklığının ve PhLi (veya PhMgBr) /I stokiyometrisinin etkisi tartışılmıştır. Optimum verim, -15° de, PhLi'un eterli çözeltisine, PhLi/I mol oranı 3:1 alınarak I'in eterli çözeltisinin katılması ile elde edilmiştir. Reaksiyon için I'in mono ve dilyum türevlerinin ara ürün olarak oluştuğu bir mekanizma önerilmiştir. Amino transfer reaktifi olarak O-mesitilensülfonilhidroksilamin'in kullanılması ve çeşitli fenil bakır bileşiklerinin aminasyonu denemiştir. Bir organik bileşiğe lityum veya magnezyum türevi oluşturulması yoluyla amino grubu sokulması için I'in uygun bir reaktif olduğu sonucuna varılmıştır.

Prix de l'abonnement annuel

Turquie: 15 TL; Etranger: 30 TL.

Prix de ce numéro: 5 TL (pour la vente en Turquie).

Prière de s'adresser pour l'abonnement à: Fen Fakültesi
Dekanlığı Ankara, Turquie.