PYRIDYLSILANES IN THE SYNTHESIS OF HETEROCYCLES (REVIEW)

É. Lukevits and I. D. Segal

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The desilylation of pyridylsilanes and pyridylmethylsilanes is one of the most characteristic reactions of organosilicon derivatives of pyridine, and it has been shown to be possible to utilize this reaction in organic synthesis. In many instances, desilylation affords difficultly-accessible pyridine derivatives, which have also been synthesized by insertion of aldehydes into the Si—C bond in pyridylsilanes and reactions of organosilicon pyridinium compounds. 2-Trimethylsilylmethylpyridine has been found to undergo the largest number of reactions leading to the formation of a variety of compounds containing the pyridine ring.

Studies of the properties of pyridylsilanes have revealed a number of features which have subsequently been used to develop novel methods of goal-oriented synthesis of difficultly accessible pyridine derivatives. For example, studies of the physical properties of pyridylsilanes have provided data which may be interpreted in terms of the +I effect of the SiR_3 group and the possible reaction of the π-electrons of the heterocycle with the vacant 3d orbitals of silicon. For instance, measurements of the basicities of pyridines with R_3Si groups in positions 2, 3, and 4 (by potentiometric titration in aqueous methanol at 25°C) have shown that they are all stronger bases than pyridine. This is satisfactorily explained by the +I effect of the heteroorganic substituent [1]. The increase in basicity of 2-Me_3M derivatives in the sequence Si (6.63) ≈ Ge (6.64) < Sn (7.57) may also be attributed to the greater electron-donor capacity of the R_3M group [1]. The much greater basicity of 2-trimethylsilylpyridine as compared with its 4-analog (pK_a 6.63 and 5.57 respectively), in contrast to 2- and 4-alkylpyridines, the pK_a values of which are usually similar (specifically, the pK_a values of 2- and 4-tert-butylpyridines are 5.76 and 5.99), has been attributed [1] to an additional effect, namely complexation during the measurement of the pK_a in methanol. However, the basicity of 4-trimethylsilylpyridine is lower than that of 4-tert-butylpyridine, suggesting that p_π—d_π-interactions make an important contribution. This decrease in basicity is even more apparent in 4-substituted pyridine N-oxides [2].

It has been shown by ^{13}C NMR that the introduction of the trimethylsilyl group into the 2, 3, or 4-position in pyridine results in a shift to lower field of the signal for ^{13}C carbon directly bonded to silicon, the greatest shift being observed in the 2-derivative [3]. At the same time, the silicon atom in 2-trimethylsilylpyridine is more strongly screened than in the 3- and 4-derivatives, the chemical shifts for ^{29}Si being −5.68, −4.10, and −3.25 ppm respectively [3].

Evidence for the existence of an inverse π → Si donor effect, reducing the energy of the π-orbital and thereby partially compensating for the inductive effect of the trimethylsilyl group, is provided by the ionization potentials of 2- and 4-tert-butyl- and trimethylsilyl-substituted pyridines, measured by photoelectronic spectroscopy [4], and by IR spectroscopic data for 4-substituted pyridine N-oxides [5].

Simultaneously with the observation of dualistic properties in organosilicon substituents in pyridines, the question arose of the display of these features in chemical reactions. Unfortunately, no quantitative data have yet been published on the effect of the pyridine ring on the reactivity of silicofunctional substituents and the influence of the latter on the reactivity of the pyridine ring or of carbofunctional groups attached thereto. However, many reactions involving the Si—C bond take place with great ease, and these are not always explicable in terms of the physicochemical data given above. This is above all true for the desilylation reaction.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006.
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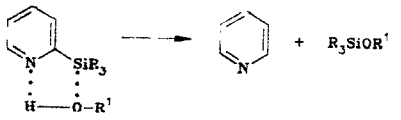
2-Trimethylsilylpyridine reacts readily with water, methanol, and ethanol to give pyridine and trimethylsilanol or the trimethylalkoxysilane [6-10], the relative rates of desilylation in water, methanol, and ethanol being 74:12:1 [7]. Higher alcohols fail to undergo this reaction. Hydrolysis of 2-trimethylsilylpyridine takes place more rapidly in alkaline than in acid media [7-9]. It has been found that at low pH values the reaction is accelerated in the presence of fluoride ions [9]. On the basis of various observations (the first order of the reaction in silane, the high entropy of activation, and the absence of an isotope effect of the solvent), it has been suggested that desilylation takes place via a five-membered cyclic complex formed by nucleophilic attack on the silicon atom by the oxygen of the solvent [6-8]:



The proposed mechanism is also supported by the observation that hydrolysis and methanolysis of 2-[methylphenyl(1-naphthyl)silyl]pyridine takes place with retention of configuration [11]. Subsequently however, on the basis of photoelectronic spectra and measurement of ionization potentials, it was suggested [9] that the predominant mechanism of hydrolysis involves nucleophilic attack by the hydroxyl ion on the trimethylsilyl group in the N-protonated heterocycle, resulting in the cleavage of a pyridinium ion.

The rate of methanolysis of 2-triorganylsilylpyridines decreases, depending on the radicals attached to silicon, in the following order: dimethyl > trimethyl > triphenyl > triethyl [12], which does not correspond to the order of changes in basicity. The rate of cleavage of the Si—C bond in methyl-substituted 2-trimethylsilylpyridines [2-$Me_3Si(RC_5H_3N)$] by water decreases depending on the position of the methyl group (position of R and relative rate of desilylation at 30.2°C given): 4-Me (1.70) > 6-Me (1.59) > 3-Me (1.58) > H (1) > 5-Me (0.71) [8, 13]. The same sequence is for the most part found in methanol, an exception being 2-trimethylsilyl-3-methylpyridine, which is in this instance less reactive [8, 13].

2-Trimethylsilylpyridine is hydrolyzed much more rapidly than 2-trimethylgermanylpyridine, but more slowly than 2-trimethylstannylpyridine [6, 8], the relative rates of hydrolysis of the Si-, Ge-, and Sn-derivatives being $1:10^{-4}:22$ [6].

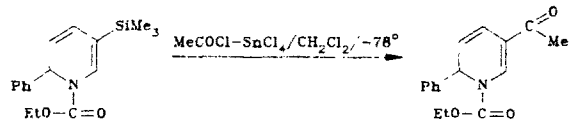
The cleavage of the $Si—C_N$ bond in trimethylsilylpyridines and -quinolines by sodium hydroxide in 4:1 $Me_2SO—H_2O$ at 50°C has been examined [14]. Quinoline derivatives are desilylated more rapidly, especially 4-trimethylsilylquinoline. The relative reaction rates vary in the sequence: 4-Q (184) > 2-Q (15.9) > 3-Q (12.7) > 4-Py (8.4) > 3-Py (2.9) > 2-Py (1.0).

Basic hydrolysis of 4-(trimethylsilyl)- and 4-(dimethylsilyl)tetrachloropyridines in THF affords 2,3,5,6-tetrachloropyridine (70%) [15]. 2-(1-Trimethylsilyl-2-phenylethyl)pyridine is hydrolyzed by 5% potassium hydroxide in aqueous ethanol at room temperature in 49 h to give 55% of 2-(β-phenylethyl)pyridine [16]. Desilylation by acid is seen with 3-trimethylsilylpyridines carrying an amino-group in positions 2, 4, or 6 [17]. Hydrolysis of 3-trimethylsilyl-2-quinoline by acid also results in cleavage of the trimethylsilyl group [18]. 2-Trimethylsilyl-3-methyl- and 2-trimethylsilyl-3-bromo-5,6,7,8-tetrahydroquinolines are readily and quantitatively desilylated at 50°C by tetramethylammonium fluoride in methanol [19].

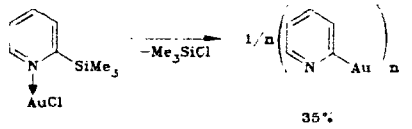
Friedel-Crafts acylation of pyridines takes place with difficulty as a result of bonding of the catalyst (Lewis acids) with the nitrogen atom, resulting in an increase in the electron deficiency of the ring and its resistance to electrophilic attack [20]. However, the Si—C bond in pyridylsilanes is readily attacked by acyl halides and chloroformate esters (probably by a four-membered cyclic mechanism), making it possible to synthesize 2-benzoylpyridine and ethyl pyridine-2-carboxylate under relatively mild conditions to give preparative yields (50-70%) [21].

R = Ph (100°, 2 h OEt (20°)

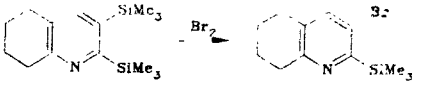
Desilylation of N-substituted 2-phenyl-5-trimethylsilyl-1,2-dihydropyridines by treatment with acetyl chloride takes place at low temperatures (−78°C) in the presence of a Lewis acid (35%) [20]:



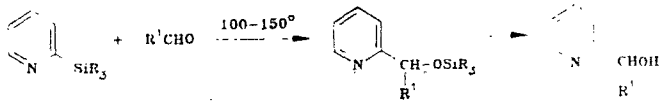
The Si—C bond in the complex of 2-trimethylsilylpyridine with gold(I) chloride is much less reactive than in the free pyridylsilane. For example, this complex is stable to hydrolysis. However, it loses trimethylchlorosilane in boiling benzene [22]:



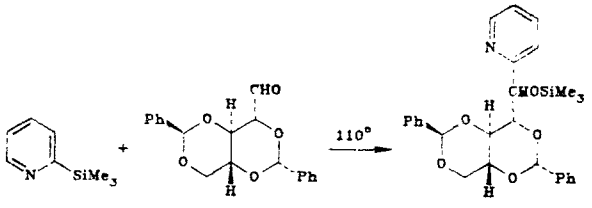
2,3-Bis(trimethylsilyl)-5,6,7,8-tetrahydroquinoline is brominated by bromine in carbon tetrachloride at room temperature exclusively in the 3-position (71%) [19]:



Organometallic derivatives of pyridine (PyMgCl and PyLi) react nonselectively with ketones and esters. Of special significance, therefore, for the synthesis of pyridylcarbinols is the ability of the C—Si bond in pyridylsilanes to undergo insertion reactions with aldehydes. For example, aldehydes react with 2-triorganylsilylpyridines at 100-150°C to give siloxyalkylpyridines (45-90%), which are readily converted by hydrolysis into the corresponding carbinols [21, 23, 24].



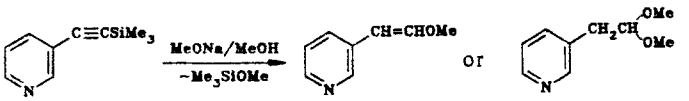
The increased reactivity of the Si—C bond in 2-trimethylsilylpyridine renders it possible to use this compound for the synthesis of C-nucleosides (for example, with 2,4:3,5-di-O-benzylidenealdehydo-D-ribose) [25, 26]:



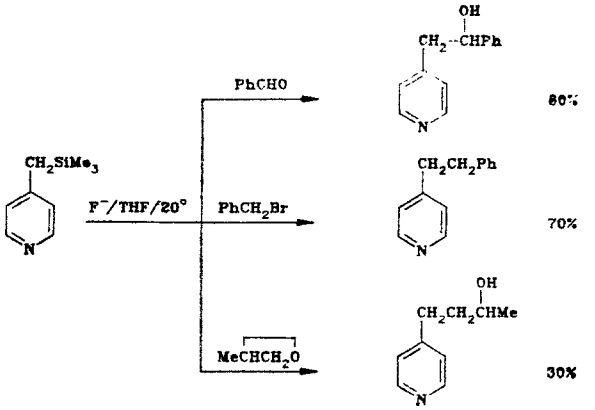
The Si—C bond in 2-trimethylsilylmethylpyridine is cleaved by 95% aqueous ethanol to give hexamethyldisiloxane, but unlike 2-trimethylsilyl-pyridine prolonged heating is required. The reaction is catalyzed by bases and especially by acids [27, 28]. The rate of reaction decreases in the sequence: 4-trimethylsilylmethylpyridine > 2-trimethylsilylmethylpyridine > 2-bis(trimethylsilyl)methylpyridine [27]. The differences in the rates of hydrolysis of the last two compounds are particularly large in acidic media, probably as a result of steric factors which hinder the protonation of the nitrogen, preceding attack on silicon.

The relative rates of cleavage of trimethylsilylmethylpyridines and -quinolines in aqueous methanolic (1:9) sodium methoxide have been measured at 50°C. They decrease in the sequence: 2-QCH_2 (41) > 4-QCH_2 (37) > 4-$PyCH_2$ (8.9) > 2-$PyCH_2$ (1.0) > 3-QCH_2 (0.161) > 3-$PyCH_2$ (0.030) [14]. In this case, as with the compounds containing the trimethylsilyl group directly attached to the ring, quinolines undergo desilylation more rapidly than the corresponding pyridines. Compounds containing the trimethysilyl group in the 3-position are the least reactive.

On treatment with sodium alkoxides in boiling alcohol, cleavage of the trimethylsilyl group occurs in some trimethylsilylethynyl derivatives of pyridine, cyanopyridines, and 2,6-dimethyl-3-nitropyridine, with the formation of the corresponding enol ether or acetal [29, 30]:

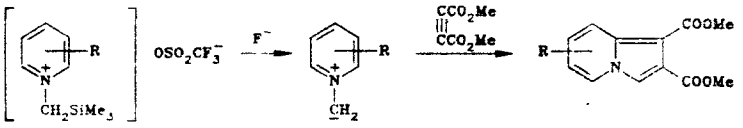


If, however, the hydrolysis of trimethylsilylethynylpyridines, -quinolines, and -isoquinolines is carried out with aqueous alcoholic KOH at room temperature, the ethynylheterocycles are obtained [31].



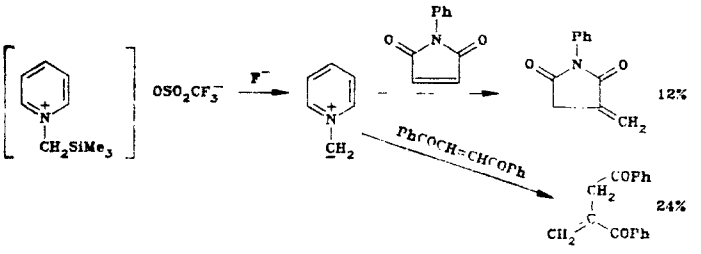
Treatment with fluoride ion results in the cleavage of the Si—C bond in 4-trimethylsilylmethylpyridine to give the carbinol. Thus, 4-trimethylsilylmethylpyridine reacts with electrophiles in the presence of KF/18-crown-6 or Bu_4NF/SiO_2 under mild conditions with cleavage of the trimethylsilyl group [32].

Treatment of N-trimethylsilylmethylpyridinium trifluoromethanesulfonate with cesium fluoride, a source of active fluoride ions, liberates the unstable pyridinium methylide [33, 34], which reacts with dimethyl acetylenedicarboxylate at 0°C to give dimethyl indolizine-1,2-dicarboxylate (31%). The use of tetrabutylammonium fluoride in dimethoxyethane at 0°C, or in THF at 0°C, as the reagent for cleaving the Si—C bond affords the same product [35]:

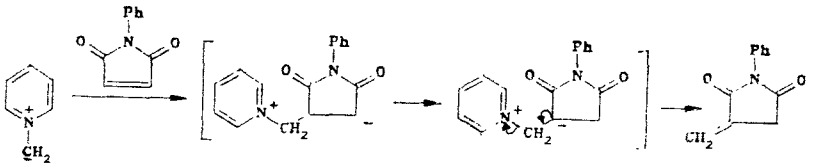


A similar reaction takes place between the corresponding derivatives of quinoline or isoquinoline and dimethyl acetylenedicarboxylate at 0°C in dimethoxyethane, in the presence of tetrabutylammonium fluoride (yields 36 and 23%, respectively) [34].

N-Trimethylsilylmethylpyridinium trifluromethanesulfonate reacts with N-phenylmaleimide under the same conditions, to give N-phenylitaconimide instead of the expected tetrahydroindolizine, and the reaction with E-1,2-dibenzoylethylene affords 2,3-dibenzoylpropene [34].

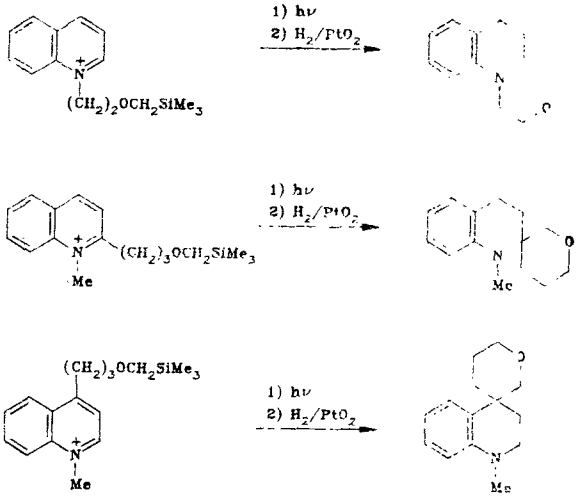


A possible mechanism for this reaction is by Michael addition of the pyridinium methylide to the olefin to give an intermediate which undergoes 1,2-proton migration followed by elimination of pyridine [34]:



It has also been observed [35] that pyridinium methylide reacts with olefins to give higher homologs of the olefins, in which the double bonds are saturated and the new C=C bonds formed.

Irradiation of [(trimethylsilylmethoxy)alkyl]quinolinium perchlorates in acetonitrile gives radicals from which new heterocyclic rings may be obtained [36]. The dihydroquinolines obtained by hydrogenation (PtO_2) are converted into more stable compounds containing the tetrahydroquinoline ring (in 41-61% yields).



A number of reactions of the lithium derivative of 2-trimethylsilylmethylpyridine (I), $PyCHLiSiMe_3$ (obtained by treatment with lithium diisopropylamide in THF at −75 to −90°C) have

Diagram 1

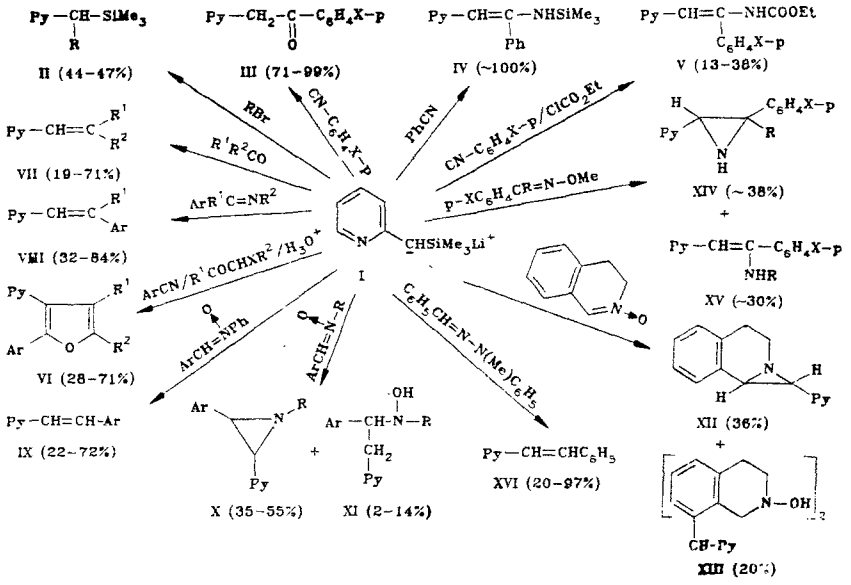
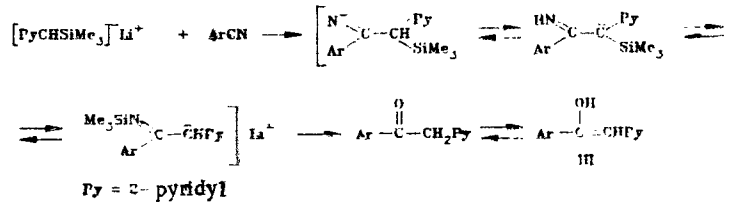
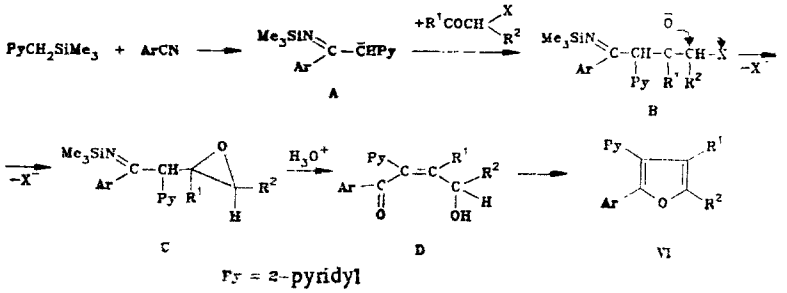


Diagram 2



Py = 2-pyridyl

Diagram 3



Py = 2-pyridyl

been examined (Diagram 1). The lithium derivative of 2-trimethylsilylmethylpyridine reacts with allyl and benzyl bromides with retention of the trimethylsilyl group (II) [16], but in many other instances desilylation takes place.

The reaction with one equivalent of a para-substituted benzonitrile results in the formation of 2-phenacylpyridines (III) [37], but when α-picoline is used in place of 2-trimethylsilylmethylpyridine, the yield of (III) is lower [37]. The suggestion [37] that intermediate tautomeric anions are formed is supported by the observation that reaction with benzonitrile gives a quantitative yield of a mixture of E- and Z-1-phenyl-2-(2-pyridyl)-1-trimethylsilylaminoethenes (IV) in a ratio of 4:1 [38]. Formation of intermediate products is shown in more detail in Diagram 2 [38].

On further reaction with ethyl chloroformate, the intermediate anions give a mixture of the E- and Z-isomers of ethyl [N-(1-aryl-2-(2-pyridyl)-ethenyl)]carbamates (V) [39]. If a halogenated ketone is present in the reaction with p-substituted benzonitriles, cleavage of the trimethylsilyl group is accompanied by the formation of the furan ring with a pyridine substituent (VI) [38]. A proposed pathway for the formation of these compounds via the anionic intermediates A, obtained by reaction of 2-trimethylsilylpyridine with the benzonitrile in the presence of lithium diisopropylamide, is shown in Diagram 3. Attack of the anions A on the carbonyl carbon of the α-haloketone gives compounds B, which undergo intramolecular nucleophilic substitution giving the oxiranes C, which are converted on treatment with hydrochloric acid into the furans (VI) via the intermediates D.

The lithium derivative reacts with ketones to give 2-(1-alkenyl)pyridines (VII) [16]. Reaction of the α-silylcarbanion with E-aldimines of anilines takes place stereospecifically to give E-2-alkenylpyridines (VIII) [40]. On reaction with α,N-diarylnitrones, instead of the expected aziridines and/or hydroxylamines, the E-alkenes (IX) were isolated together with azobenzene and/or azoxybenzene [41]. With α-aryl-N-alkylnitrones, α,N-dialkylnitrones, and cyclic nitrones, the principal products were the aziridines (X) and (XII), in some cases accompanied by the hydroxylamines (XI) and (XIII) [41]. The reaction with the methyl ethers of para-substituted benzaldoximes is fully stereospecific, giving trans-2-aryl-3-(2-pyridyl)-azidines (XIV) and Z-1-amino-1-aryl-2-(2-pyridyl)ethenes (XV) [42]. Reaction of the α-silylcarbanion with benzyldehyde phenylhydrazone in the presence of crown ethers [2.1.1]cryptand, or polyglymes in THF at −75°, 0°, or at the boil, gives the E- or Z-α-stilbazoles (XVI) [43].

These examples therefore show that pyridylsilanes and pyridylmethylsilanes may be advantageously employed in the synthesis of a wide variety of heterocycles. The development of convenient methods for the preparation of the pyridylsilanes has contributed to this end. The most general method involves the reaction of lithio-, sodio-, potassio-, or organomagnesium derivatives of pyridines with organylchlorosilanes or organyl(chlororganyl)silanes. Extensively used are the lithio-derivatives, obtained by reacting the halopyridine or methylpyridine with organolithium compounds RLi [2-4, 12-14, 17, 21, 44-50]. In some instances, the unsubstituted pyridine has been silylated [51-53]. Lithium diisopropylamide is being

used with increasing frequency as the metallating agent [14, 37, 54, 55]. The Grignard reaction has been employed for the preparation of silylated pyridines [6, 7, 14, 15, 56, 57]. Other methods of preparation have also been reported. Methods of synthesis of organosilicon compounds of pyridine have been discussed in greater detail in review [58].

The possibilities for the use of organosilicon derivatives of pyridine in organic synthesis are far from being exhausted. Insertion reactions at the C—Si bond, photochemical cyclizations, and desilylation followed by further reactions of the intermediate anions could find extensive application in the synthesis of a wide variety of nitrogen heterocycles.

LITERATURE CITED

1. D. G. Anderson, J. R. Chipperfield, and D. E. Webster, J. Organomet. Chem., 12, 323 (1968).
2. M. A. Weiner and P. Schwartz, J. Organomet. Chem., 35, 285 (1972).
3. T. V. Mitchell, Org. Magn. Reson., 7, 610 (1975).
4. E. Heilbronner, V. Hornung, F. H. Pinkerton, and S. F. Thames, Helv. Chim. Acta, 55, 289 (1972).
5. M. A. Weiner and M. Lattman, Tetrahedron Lett., No. 18, 1709 (1974).
6. D. G. Anderson and D. E. Webster, J. Chem. Soc., B, No. 7, 765 (1968).
7. D. G. Anderson, M. A. M. Bradney, and D. E. Webster, J. Chem. Soc., B, No. 4, 450 (1968).
8. D. G. Anderson, M. A. Bradney, and D. E. Webster, in: Intern. Symp. Organosilicon Chem., Sci. Commun., Prague (1965), p. 270; Chem. Abstr., 66, 1964 (1967).
9. R. S. Brown, J. Slebocka-Tilk, J. M. Buschek, and J. G. Ulan, J. Am. Chem. Soc., 106, 5979 (1984).
10. D. G. Anderson, M. A. M. Bradney, B. A. Loveland, and D. E. Webster, Chem. Ind., No. 12, 505 (1964).
11. D. G. Anderson and D. E. Webster, J. Chem. Soc., B, No. 8, 878 (1968).
12. D. G. Anderson and D. E. Webster, J. Chem. Soc., B, No. 9, 1008 (1968).
13. D. G. Anderson and D. E. Webster, J. Organomet. Chem., 13, 113 (1968).
14. A. Fisher, M. W. Morgan, and C. Eaborn, J. Organomet. Chem., 136, 323 (1977).
15. S. S. Dua and H. Gilman, J. Organomet. Chem., 12, 234 (1968).
16. T. Kanakahara and J. Tagaki, Synthesis, No. 3, 192 (1979).
17. Y. Sakata, K. Adachi, Y. Akahori, and E. Hayashi, J. Pharm. Soc. Jpn., 87, 1374 (1967).
18. G. Merault, P. Bougeois, and N. Duffaut, Bull. Soc. Chim. Fr., Nos. 9-10, 1949 (1974).
19. D. J. Brien, A. Naiman, and K. P. C. Vollhardt, Chem. Commun., No. 2, 133 (1982).
20. D. L. Comins and N. B. Manthlo, Tetrahedron Lett., 24, No. 35, 3683 (1983).
21. F. H. Pinkerton and S. F. Thames, J. Organomet. Chem., 24, 623 (1970).
22. P. Jutzi and H. Heusler, J. Organomet. Chem., 114, 265 (1976).
23. F. H. Pinkerton and S. F. Thames, J. Heterocycl. Chem., 6, 433 (1969).
24. T. Ogawa, M. Yasui, and M. Matsui, Agr. Biol. Chem., 34, 970 (1970).
25. T. Ogawa, M. Yasui, and M. Matsui, Agr. Biol. Chem., 36, 1443 (1972).
26. É. Ya. Lukevits, A. A. Zablotskaya, and I. I. Solomennikova, Usp. Khim., 43, 370 (1974).
27. C. Eaborn and R. A. Shaw, J. Chem. Soc., No. 9, 3306 (1955).
28. T. Kondo, K. Yamamoto, and M. Kumada, J. Organomet. Chem., 35, C30 (1972).
29. T. Sakamoto, Y. Kondo, and H. Yamanaka, Heterocycles, 22, 1347 (1984).
30. T. Sakamoto, Y. Kondo, and H. Yamanaka, Chem. Pharm. Bull., 33, 626 (1985).
31. T. Sakamoto, M. Shiraiwa, Y. Kondo, and H. Yamanaka, Synthesis, No. 4, 312 (1983).
32. A. Ricci, A. Degl' Innocenti, M. Florenza, M. Taddei, M. A. Spartera, and D. R. Walton, Tetrahedron Lett., 23, No. 5, 577 (1982).
33. O. Tsuge, S. Kanemasa, S. Kuraoka, and S. Takenaka, Chem. Lett., No. 2, 279 (1984).
34. Y. Miki, H. Hachiken, and S. Takemura, Heterocycles, 22, 701 (1984).
35. O. Tsuge, S. Kanemasa, S. Kuraoka, and S. Takenaka, Chem. Lett., No. 2, 281 (1984).
36. M. A. Brumfield, L. Quillen, Ung Chan Yoon, and P. S. Mariano, J. Am. Chem. Soc., 106, 6855 (1984).
37. T. Konakahara and Y. Tagaki, Heterocycles, 14, 393 (1980).
38. O. Tsuge, K. Matsuda, and S. Kanemasa, Heterocycles, 20, 593 (1983).
39. T. Konakahara, A. Watanabe, and K. Sato, Heterocycles, 23, 383 (1985).
40. T. Konakahara and Y. Tagaki, Tetrahedron Lett., 21, No. 21, 2073 (1980).
41. O. Tsuge, K. Sone, S. Urano, and K. Matsuda, J. Org. Chem., 47, 5171 (1982).
42. T. Konakahara, M. Matsuki, and K. Sato, Heterocycles, 22, 1319 (1984).

43. T. Konakahara, H. Nishigaki, A. Watanabe, and K. Sato, Heterocycles, 22, 2765 (1984).
44. I. Haiduc and H. Gilman, Rev. Roum. Chim., 16, 597 (1971).
45. W. K. Musker and R. L. Scholl, J. Organomet. Chem., 27, 37 (1971).
46. I. Katz, British Patent No. 757,855; Chem. Abstr., 51, 15,600 (1957).
47. L. H. Sommer, US Patent No. 2,838,515; Ref. Zh. Khim., 83,215 (1959).
48. G. P. Gisby, S. E. Royall, and P. G. Sammes, J. Chem. Soc., Perkin Trans. I, No. 1, 169 (1982).
49. R. I. Papasergio, C. L. Taston, and A. H. White, Chem. Commun., No. 23, 1419 (1983).
50. N. V. Bac and Y. Langlois, J. Am. Chem. Soc., 104, 7666 (1982).
51. J. Verbeek, Y. V. E. George, L. P. de Jong, and L. Brandsma, Chem. Commun., No. 4, 257 (1984).
52. J. Verbeek and L. Brandsma, J. Org. Chem., 49, 3857 (1984).
53. D. Wittenberg and H. Gilman, Chem. Ind., 390 (1958).
54. F. Marsais and G. Queginer, Tetrahedron, 39, 2009 (1983).
55. F. Marsais, B. Laperdrix, T. Güngör, M. Mallet, and G. Queiginer, J. Chem. Res., M, No. 10, 2863 (1982).
56. F. Effenberger and D. Häbich, Lieb. Ann. Chem., No. 6, 842 (1979).
57. British Thomson-Houston Co. Ltd., British Patent No. 685,186; Chem. Abstr., 28, 2783 (1954).
58. É. Ya. Lukevits and I. D. Segal, Pyridine and Quinoline Derivatives of Group IVB Elements. Preprint [in Russian], Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga, Part 1 (1986).

ROTATIONAL ISOMERS OF THE RADICAL-ANIONS OF 2-CARBONYL-CONTAINING DERIVATIVES OF 5-NITROFURAN

R. A. Gavar, L. Kh. Baumane, Ya. P. Stradyn', M. B. Fleisher, M. Chernaeva*, and Ya. Kovach

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The radical-anions of 2-carbonyl-containing derivatives of 5-nitrofuran were obtained by electrochemical generation. Their ESR spectra indicate the existence of a mixture of O,O-cis and O,O-trans rotational isomers. The parameters of the isomers were identified by INDO calculations. The more polar form (the cis isomer) is more stable in polar media.

Published data on the ESR spectra of the radical-anions of 2-carbonyl-containing derivatives of 5-nitrofuran do not give any information on the stereochemical orientation of the carbonyl-containing substituent in relation to the furan ring. As a rule, an ESR spectrum with a hyperfine structure (hfs) characterizing only one type of structure in the corresponding radical-anion is obtained for each investigated compound [1-4]. This can evidently be explained by the low stability of these radicals [5].

At the same time such radical-anions with a planar structure can be represented in the form of two rotational isomers:

O,O-cis O,O-trans

*Deceased

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Slovak Higher Technical School, Bratislava, Czechoslovakia 81237. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 14-21, January, 1987. Original article submitted July 2, 1986.

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