HETEROCYCLES, Vol 20, No 7, 1983

SYNTHESIS AND PREPARATIVE APPLICATIONS OF MONOSACCHARIDE THIOCYANATES

Zbigniew J. Witczak*
Department of Organic Chemistry, Medical Academy
Faculty of Pharmacy, 90-145 Łodz, Narutowicza 120A Poland

Abstract - This review describes the synthetic methods which have been developed for the preparation of monosaccharide thiocyanates as well as their transformation to derivatives such as deoxysugars thiosugars.

Contents

1. INTRODUCTION

Sugar thiocyanates have been readily synthesized by a variety of methods using as a starting material the corresponding halides.[1,2] These methods often show a striking parallel with those used for making the corresponding halides, thus reflecting the marked pseudohalide character of the thiocyanate group.[3] This pseudohalide character of the thiocyanate anion however differs from halide anions in that it is an ambident[4] nucleophile due to resonance.

$$-\overset{\curvearrowright}{\bar{S}}-C\equiv N \;\text{———}\; S=C=N$$

which results in a resonance hybrid and the charge distribution is as shown.[5]

$$\begin{array}{ccccc} -0.7108 & & -0.1934 & & -0.4826 \\ S & \text{-----------} & C & \overline{\overline{\text{-----------}}} & N \end{array}$$

Consequently, kinetically controlled reactions of the thiocyanate anion with organic compounds (among them halides) may lead either to the thiocyanates by nucleophilic attack of the sulphur atom, or to the isothiocyanates by nucleophilic attack of the nitrogen atom or to a mixture of both. The thermodynamically more-stable isothiocyanate may also be formed by a secondary isomerization reaction. In common with other ambident species[6] the relative nucleophilicity K_S/K_N[7] of the sulfur and nitrogen of the thiocyanate anion may depend on the interplay of

---

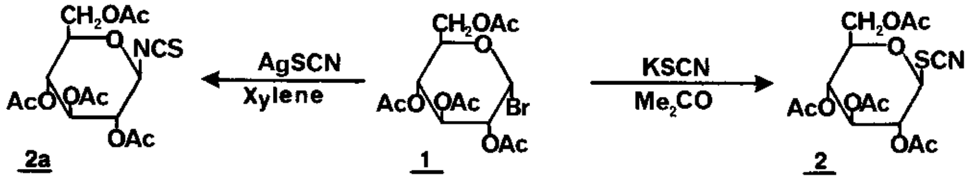
*Present address for correspondence: Food Sciences Institute, Purdue University, West Lafayette, Indiana 47907 U.S.A.

different factors, i.e. solvent, catalyst, counter-ions, temperature, nature of leaving group, concentration and, of course, the structure of the organic compound (particularly the geometry of the molecule). Physico-chemical methods e.g. IR[8] and NMR[9] spectroscopy, now permit rapid detection of isothiocyanate coproducts, which may be readily removed by chemical as well as chromatographic methods.[10]

Ability of the thiocyanate group to react either as a pseudohalide group or as sulphenyl cyanide provides attractive approaches to many types of derivatives, particularly N- and S-heterocycles. The fact that the chemistry of sugar thiocyanates is relatively little known in contrast to its potential application in the synthesis of deoxysugars and thiosugars encouraged review of the literature in this field.

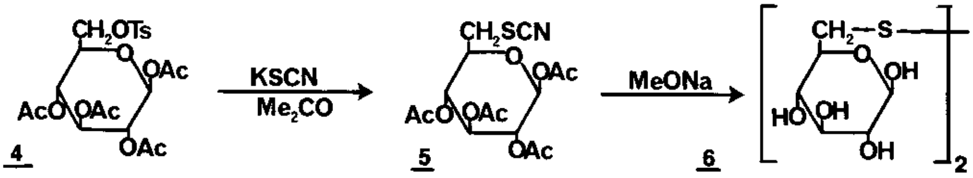
2. METHOD OF PREPARATION OF MONOSACCHARIDE THIOCYANATES AND THEIR APPLICATION

The first sugar thiocyanate was synthesized by Müller and Wilhelms[2] in 1941 by the treatment of 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide (1) with potassium thiocyanate in anhydrous acetone, whereas isomeric isothiocyanate has been synthesized by Emil Fischer[1] in 1914 by the treatment of (1) with silver thiocyanate in anhydrous xylene.



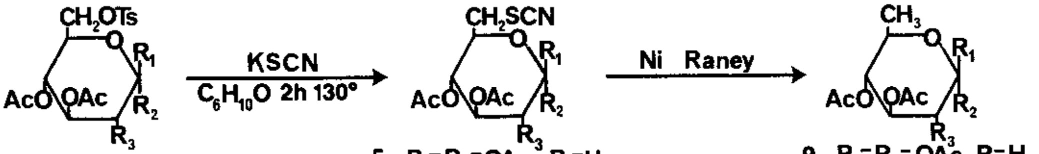
Fischer[11] also prepared 1,6-dideoxy-6-bromo-1-isothiocyanato-2,3,4-tri-O-acetyl-α-D-glucose similarly. Later Müller and Wilhelms[2] applied the Fischer method to the preparation of 6-deoxy-6-thiocyanato-α-D-glucopyranosyl bromide (3), and examined the problem of the isomerization of the thiocyanate to the isothiocyanate derivatives of D-glucose. They also prepared both α and β methylglucosides of 6-deoxy-6-thiocyanato-D-glucose.

Moreover, they also first applied nucleophilic displacement of the p-tolylsulfonate group by the thiocyanate ion in anhydrous acetone (10 h in sealed tube at 130°) for the preparation of 6-deoxy-6-thiocyanato-1,2,3,4-tetra-O-acetyl-α-D-glucose (5) which was an intermediate to disulfide (6)



The above method of preparation of sugar thiocyanates via nucleophilic S_N2 displacement of sulfonyloxy group has been reported by a number of authors.[12-13,15-36]

Nucleophilic displacement of sugar sulfonate groups by various nucleophiles has also been reported in reviews by Richardson[14a] as well as Ball and Parrish[14b], taking into consideration all the factors influencing reactivity in reactions, particularly geometry of the molecule and the nucleophilicity of the attacking group. Stanek and Tajmr [12,13] have applied this method for the preparation of chinovose derivatives (9) and (10).

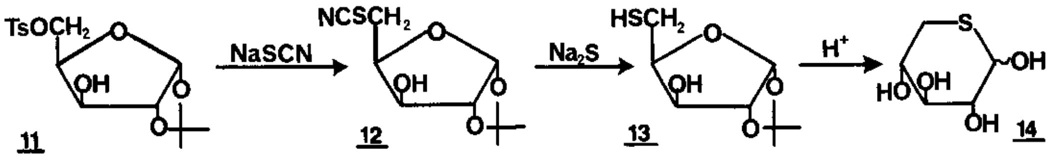


4 R_1=OAc R_2=H R_3=OAc
7 R_1=H R_2=OAc R_3=OTs

5 R_1=R_3=OAc R_2=H
8 R_1=H R_2=OAc R_3=OTs

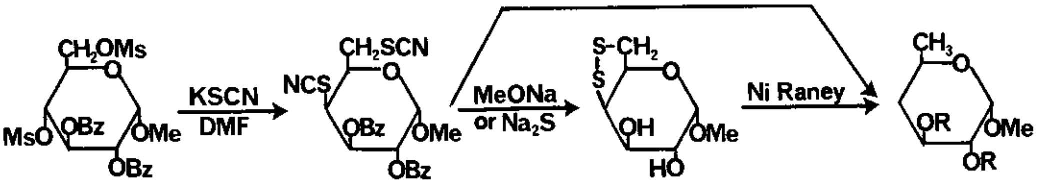
9 R_1=R_3=OAc R_2=H
10 R_1=H R_2=OAc R_3=OTs

Schwarz and Yule[15] reported S_N2 displacement of the 5-p-tolylsulfonyl group in 1,2-O-isopropylidene-5-O-tolylsulfonyl-α-D-xylofuranose (11) as a first step in the synthesis of 5-thio-D-xylopyranase (14).



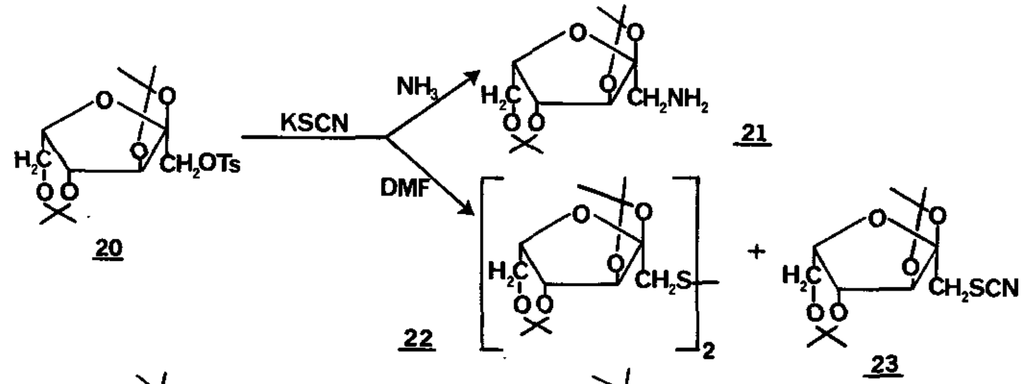
11 12 13 14

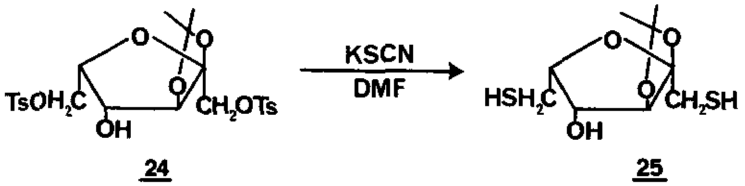
Hill, Hough and Richardson[16] have prepared methyl 4,6-dideoxy-4,6-dithiocyanato-α-D-galactopyranoside (16) via the S_N2 reaction of the methanesulfonyloxy group in (15) with thiocyanate ion in DMF. Intermediates (16) and (17) could clearly also be used for preparing deoxysugars (18) and (19) by desulfurization with Raney nickel.



15 16 17 18 R=H 19 R=Bz

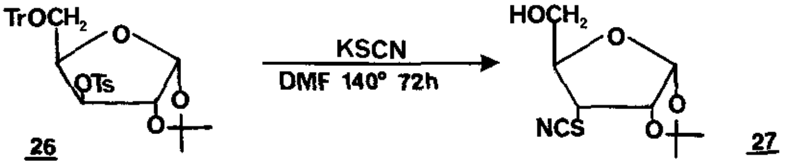
Tokuyama and coworkers[17,18] report the displacement of the p-tolylsulfonate group in 1-O-p-toluenesulfonyl-2,3,4,6-di-O-isopropylidene-α-L-sorbofuranose (20) and 1,6-di-O-p-toluenesulfonyl-2,3-O-isopropylidene-α-L-sorbofuranose (24) in liquid ammonia as well as in dimethylformamide with the thiocyanate ion.



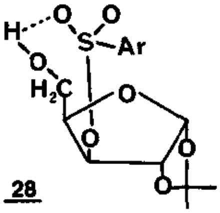


Treatment of (20) with potassium thiocyanate in DMF gives, instead of the thiocyanato sugar the disulfide (22) which was considered to be formed by the decomposition of the intermediate thiocyanato sugar.

Nucleophilic displacement of p-tolylsulfonate groups at position C-3 (usually highly resistant towards S_N2 displacement) in the furanose ring with inversion of configuration has been reported by Defaye and Hildesheim.[19]

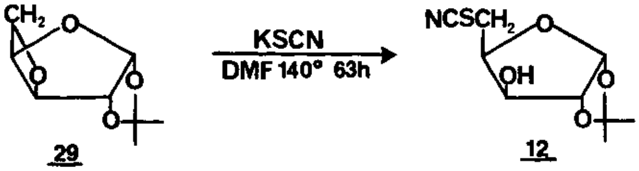


This displacement occurs much more readily than that of the corresponding 5-O-trityl (26) and 5-deoxy-derivatives. It was suggested that intramolecular electrophilic assistance was provided by the hydroxyl group at C-5 as shown in (28) and would facilitate development of a negative charge on the sulfonate in the transition state.



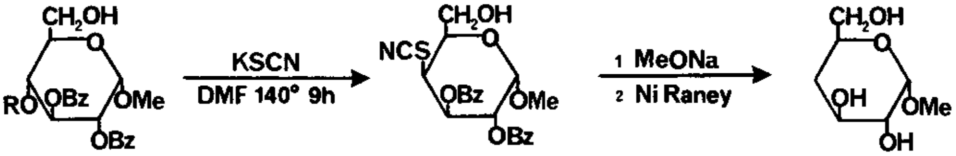
28

Treatment of anhydrosugar (29) with potassium thiocyanate produced the stable crystalline thiocyanate (12) in 12% yield.



29 12

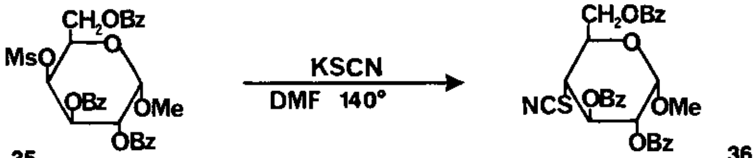
Cook and Overend[20] report the S_N2 displacement of a sulfonyloxy group at the C-4 position of a D-glucose derivative (31) with thiocyanate ion to yield a 4-substituted galacto-derivative (33) which was an intermediate to the deoxy-sugar (34), obtained by desulfurization with Raney nickel.



31 R= Ts
32 R= p-$BrC_6H_4SO_2$
33
34

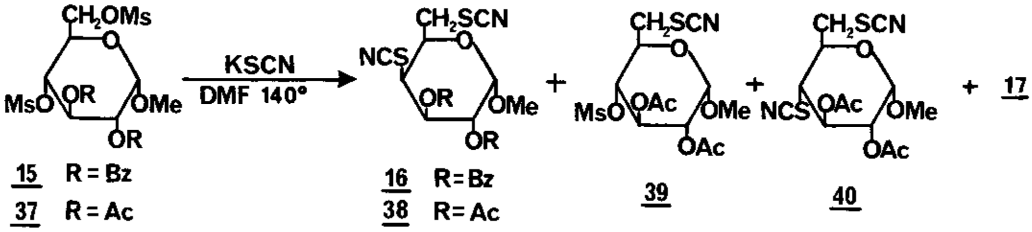
Displacement of the p-bromosulfonyl group in (32) gave (33) in improved yield (55%) after only 2.5 h of heating.

Also in the C-4 position Oven and Ragg[24] have tried the same reaction on the corresponding β-D-galactoside and other 4-O-methanesulfonyloxy and 4-O-p-tolylsulfonyl-β-D-galactosides without success. However, Gero and Guthrie[22] prepared methyl 4-deoxy-4-thiocyanato-α-D-glucopyranoside (36) by S_N2 displacement of the methanesulfonyloxy group by thiocyanate ion in DMF (46 h at 140°) in 56% yield. They confirmed by ^1H NMR spectroscopy the gluco-configuration in a D-C_1 conformation. Kochetkow and coworkers[23-24] as well as Vegh and Hardegger[25] also prepared the C-4 thiocyanate (36) as a starting material for the preparation of uridine diphosphate-4-deoxyglucose[23] as well as 4-thio-α-D-glucopyranosyl phosphate[24] and the corresponding deoxysugar (34).[25]

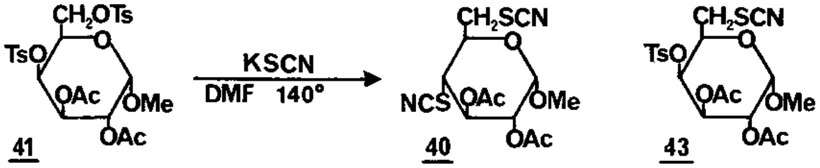


35 36

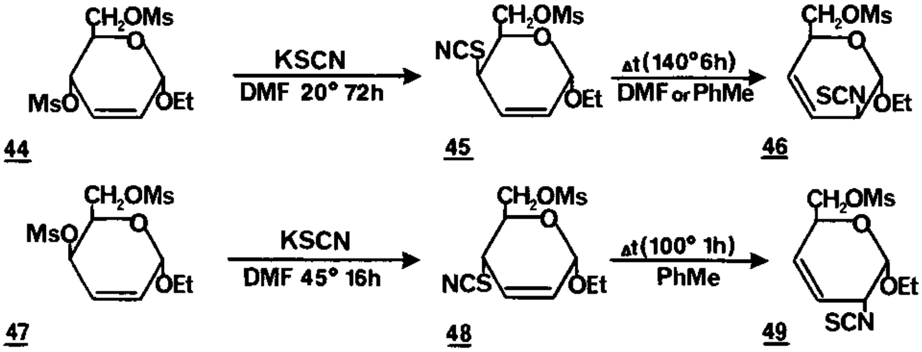
Under similar conditions to those described in the literature[22] and in contrast to previous reports[16], the 2,3-diacetate and 2,3-dibenzoate of methyl 4,6-di-O-mesyl-α-D-glucopyranoside, (15) and (37), afforded the corresponding 4,6-dideoxy-4,6-dithiocyanato-α-D-galactopyranosides[26], (16) and (38), together with a small amount of the thiocyanates (39) and (40), as well as disulfide (17)[16], which is probably formed by hydrolysis of dithiocyanate (38).



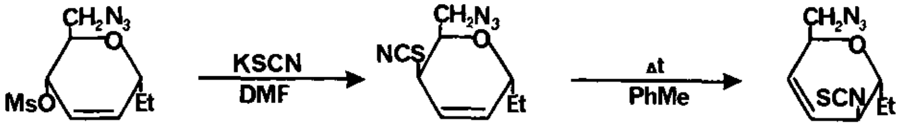
Treatment of ditosylate (41) under the same conditions affords a mixture of mono- and di-thiocyanates (40) and (43) in the ratio 1:1 but in only 50% yield because of excessive decomposition of starting material.



Ferrier and Vehtaviyasar[27-28] report the thermal rearrangement of 2,3-unsaturated thiocyanates (45) and (48) to 3,4-unsaturated isothiocyanates (46) and (49). The starting thiocyanates (45) and (48) were prepared by S_N2 nucleophilic displacement of a methanesulfonyloxy group at the C-4 position by thiocyanate ion under unusual conditions (DMF, room temperature, 72 h) for (45) and (DMF, 45°, 16h) for (48).

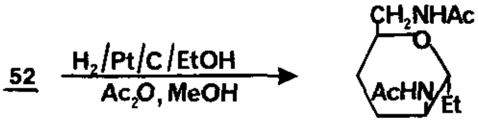


It is noteworthy that the S_N2 nucleophilic displacement reaction occurred in these cases preferentially at the secondary allylic position in contrast to the previous literature[16] detailing similar nucleophilic displacements of the 4,6-di-O-mesyl derivative (15). Guthrie and Williams[29] described the rearrangement of allylic thiocynates, using as a starting product ethyl 2,3,6-trideoxy-4-O-mesyl-6-azido-α-D-threo-hex-2-enopyranoside (50).



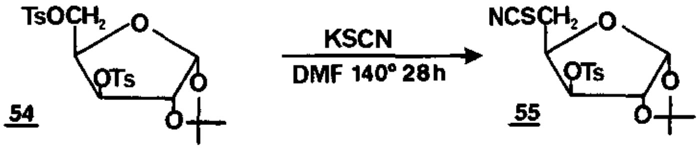
50 51 52

The isothiocyanate (52) was an intermediate in the preparation of the antibiotic branched-chain sugar D-epi-purpurosamine derivative (53) by reduction and acetylation.



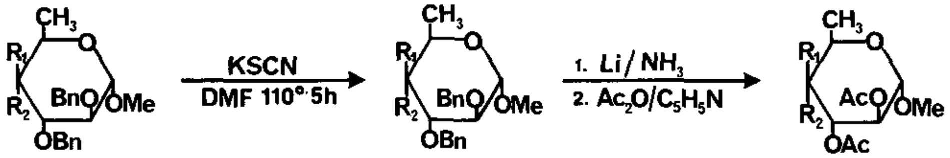
53

Owen and coworkers[30] applied S_N2 displacement of the 5-O-p-toluenesulfonate group in ditosylate (54) for confirmation of resistance of the exo-sulfonate group at the C-3 position in furanose ring, as well as for comparison of the course of this displacment by thiobenzoate and thioacetate ions. The yield of thiocyanate (55) was not comparable to earlier results.[15]



54 55

Gross and Oriez[31] reported the synthesis of 6-deoxy-4-thio-D-altrose and D-idose derivatives (60) and (61) using as a starting materials the corresponding

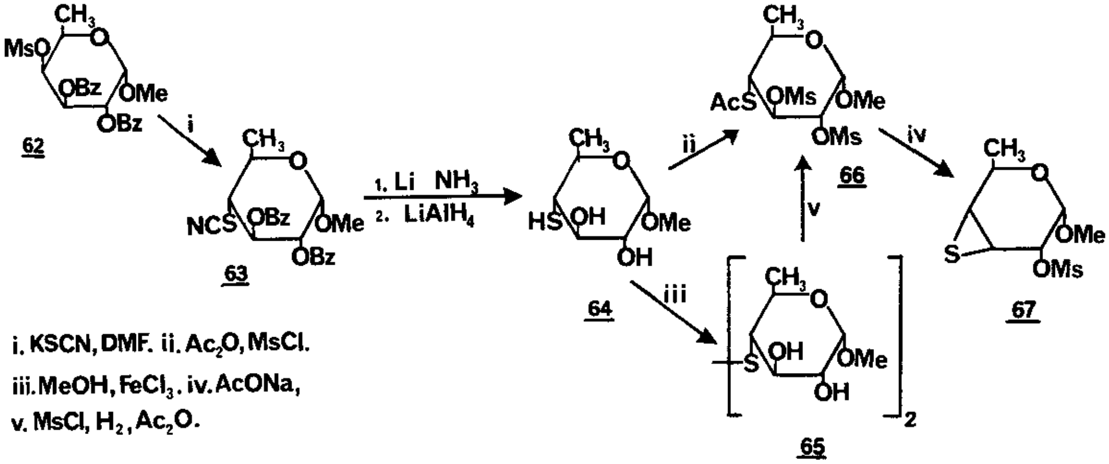


56 R_1=H R_2=OMs
57 R_1=OMs R_2=H

58 R_1=SCN R_2=H
59 R_1=H R_2=SCN

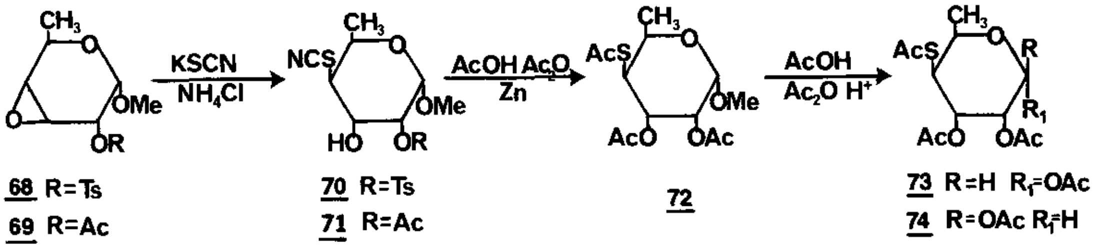
60 R_1=SAc R_2=H
61 R_1=H R_2=SAc

thiocyanates prepared from mesyl derivatives (56) *and* (57) by S_N2 nucleophilic displacement with the thiocyanate ion under standard conditions (DMF, 110°, 5h) in about 35% yield. However, they also observed the simultaneous formation of the isomeric isothiocyanate in about 5% yield. Boigegrain and Gross[32] also report an approach (via thiocyanate) to the preparation of the 3,4,6-trideoxy-3,4-epithio-α-D-allopyranoside derivative (67)



i. KSCN, DMF. ii. Ac_2O, MsCl. iii. MeOH, $FeCl_3$. iv. AcONa, v. MsCl, H_2, Ac_2O.

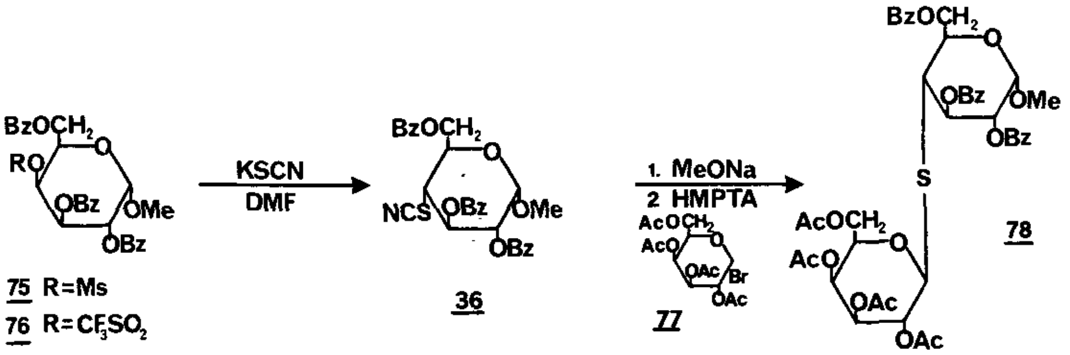
and 1,2,3-tri-O-acetyl-4-thioacetyl-6-deoxy-4-thio-D-glucopyranose derivatives (73) and (74) using the method previously applied by Dennis[33] as well as Dickerson.[34]



The approach to (73) and (74) starts from the appropriate 3,4-anhydrosugars (68) and (69) and proceeds via thiocyanates (70) and (71).

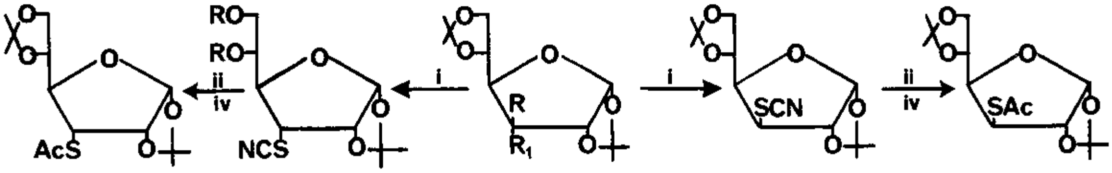
Recently Goodman group[35] reported a synthetic approach to the preparation of S-β-D-galactopyranosyl-4-thio-D-glucopyranose (78) (thiolactose) using as a starting material 4-O-mesyl-D-galactopyranoside (75) or 4-O-triflyl-α-D-galactopyranoside (76).

S_N2 nucleophilic displacement of the trifloxy group of (76) required only 12 h at 80° and provided the thiocyanate (36) in 85% yield,



whereas the mesyl group in (75) required 42 h at 140° and provided the thiocyanate (36) in 68% yield.

Recently, Philips and Goodman[36] reported the synthesis of some thiocyanates as intermediates in the synthesis of 3-thio-D-glucose (84) and 3-thio-D-allose (85) derivatives. The sequence starts from the isomeric triflates (79) and (80).



85 81 $R=Me_2C<$ 82 $R=H$ 79 $R=CF_3SO_2O$, $R_1=H$ 80 $R=H, R_1=CF_3SO_2O$ 83 84

i. KSCN-AcCN, ii. $LiAlH_4$, iv. Ac_2O

They have found that *gluco* isomer (79) affords thiocyanate (81) in low yield, whereas the *allo* isomer (80) gives thiocyanate (83) in 70% yield, when they use acetonitrile as a solvent. In the case of *gluco* isomer (79) they have also observed simultaneous formation of a partially deblocked derivative (82) as well as an unsaturated derivative i.e. 3-deoxy-1,2,5,6-di-O-isopropylidene-α-D-*erythro*-hex-3-enofuranose, probably as a result of the presence of potassium triflate in the reaction mixture under these conditions. Notably, displacements of the 3-O-p-tolylsulfonyl esters of 1,2,5,6-di-O-isopropylidene-α-D-allofuranose with the thiocyanate ion in DMF at high temperature were unsuccessful according to these authors.[36]

3. CONCLUSION

The preceding is a brief review of the preparative chemistry of monosaccharide thiocyanates, and there is much more interesting chemistry of the isomeric isothiocyanates as intermediates in the preparation of various classes of heterocyclic carbohydrate derivatives. This will be the subject of a separate review[37] and consequently discussion here is confined to the synthesis and reaction of carbohydrate thiocyanates.

Significant application of monosaccharide thiocyanates as intermediates in the preparation of deoxysugars and thiosugars derivatives was noted. However, the method employing S_N2 displacement of sulfonyloxy groups by thiocyanate ions is useful only when relatively easily displaceable groups are involved, such as mesyl group as well as the recently reported triflate leaving group.[35,36,38-41]

TABLE 1

Monosaccharide thiocyanates

Compound	m.p. 6.p°C	$[\alpha]_{25}^{D}$	Ref.
2,3,4,6-Tetra-O-acetyl-β-D-glucopyranose-thiocyanate	131-132°	-20.8°($CHCl_3$)	1,2
1,2,3,4-Tetra-O-acetyl-6-deoxy-6-thiocyanato-β-D-glucopyranose	117-118°	24° (C 2.0 $CHCl_3$)^{2} +27.9° (C 10 $CHCl_3$)^{12,13}	2,12,13
1,3,4-Tri-O-acetyl-2-O-p-tolylsulfonyl-6-deoxy-6-thiocyanato-α-D-glucopyranose	136°	+137° (C 0.6 $CHCl_3$)	12,13
Methyl 6-deoxy-6-thiocyanato-2,3,4-tri-O-acetyl-α-D-glucopyranoside	101-105°	+154.8° ($CHCl_3$)	2
Methyl 6-deoxy-6-thiocyanato-2,3,4-tri-O-acetyl-β-D-glucopyranoside	134-135°	+15.6° ($CHCl_3$)	2
2,3,4,-Tri-O-acetyl-6-deoxy-6-thiocyanato-α-D-glucopyranose bromide	160°	+212.1° ($CHCl_3$)	2
5-Deoxy-1,2-O-isopropylidene-5-thiocyanato-α-D-xylofuranose	108-110°	-16° (C Q4 MeOH)	15,19
Methyl 2,3-di-O-benzoyl-4,6-dideoxy-4,6-dithiocyanato-α-D-galactopyranoside	212-214°	+93.5° (c 0.32 $CHCl_3$)	16,26
1-Deoxy-1-thiocyanato-2,3,4,6-di-O-isopropylidene-α-L-sorbofuranose	170° (7 mm)	-10.6° (c 1.1 $CHCl_3$)	17,18
3-Deoxy-1,2-O-isopropylidene-3-thiocyanato-α-D-ribofuranose	101.5-102.5°	+50° (c 0.5 $CHCl_3$)	19
Methyl 2,3-di-O-benzoyl-4-deoxy-4-thiocyanato-α-D-galactopyranoside	132-133°	+89.4° (c 1.0 $CHCl_3$)	20
3-Deoxy-1,2-O-isopropylidene-3-thiocyanato-glycerol	51-53° (0.02 mm)	———	22
Methyl 2,3,6-tri-O-benzoyl-4-deoxy-4-thiocyanato-α-D-glucopyranoside	194-194.5°	+60.3° (c 0.53 $CHCl_3$)	22,23,24,25,36
Methyl 2,3-di-O-acetyl-4,6-dideoxy-4,6-dithiocyanato-α-D-galactopyranoside	183-185°	+134° (c 1.52 $CHCl_3$)	26

Methyl 2,3-di-O-acetyl-6-deoxy-6-thiocyanato-4-mesyl-α-D-glucopyranoside	171.5-172.5°	+150° (c 1.06 $CHCl_3$)	26
Methyl 2,3-di-O-acetyl-4,6-dideoxy-4,6-dithiocyanato-α-D-glucopyranoside	144-145°	+56° (c 1.07 $CHCl_3$)	26
Methyl 2,3-di-O-acetyl-6-deoxy-6-thiocyanato-4-O-p-tolylsulfonyl-α-D-galactoside	126-129°	+167° (c 1.96 $CHCl_3$)	26
Ethyl 2,3,4-trideoxy-6-O-mesyl-4-thiocyanato-α-D-threo-hex-2-enopyranoside	91-92°	-275° ($CHCl_3$)	27,28
Ethyl 2,3,4-trideoxy-6-O-mesyl-4-thiocyanato-α-D-erythro-hex-2-enopyranoside	85-86°	+115° ($CHCl_3$)	27,28
Ethyl 2,3,4-trideoxy-6-azido-4-thiocyanato-α-D-threo-hex-2-enopyranoside	—	—	29
5-Deoxy-1,2,-O-isopropylidene-5-thiocyanato-3-O-tolylsulfonyl-α-D-xylofuranose	—	-30° (c 1.0 $CHCl_3$)	30
Methyl 2,3,-di-O-benzyl-4,6-dideoxy-4-thiocyanato-α-D-idopyranoside	—	—	31
Methyl 2,3-di-O-benzyl-4,6-dideoxy-4-thiocyanato-α-D-altropyranoside	—	—	31
Methyl 2,3-di-O-benzoyl-4,5-dideoxy-4-thiocyanato-α-D-gulopyranoside	—	—	32,33
Methyl 4,6-dideoxy-4-thiocyanato-2-O-p-tolylsulfonyl-α-D-gulopryanoside	123-124°	—	32,33,34
Methyl 4,6-dideoxy-4-thiocyanato-2-O-p-tolylsulfonyl-3-O-trimethylsilyl-α-D-glucopyranoside	—	—	32,33,34
Methyl 4,6-dideoxy-4-thiocyanato-2-O-acetyl-α-D-gulopyranoside	—	—	32,33,34
Methyl 2,3-di-O-acetyl-4,6-dideoxy-4-thiocyanato-α-D-gulopyranoside	76-78°	+74.8° (c 1.45 $CHCl_3$)	32,33,34
3-Deoxy-3-thiocyanato-1,2,5,6-di-O-isopropylidene-α-D-allofuranose	48-50°	+63.9° (c 1.0 $CHCl_3$)	36
3-Deoxy 1,2-O-isopropylidene-3-thiocyanato-α-D-allofuranose	109-110°	+66 (c 1.0 $CHCl_3$)	36
3-Deoxy 1,2-O-isopropylidene-3-thiocyanato-5,6-di-O-acetyl-α-D-allofuranose	99-100°	+79.6° (c 1.0 $CHCl_3$)	36

3-Deoxy-1,2,5,6-di-O-isopropylidene-3-thiocyanato-α-D-glucofuranose	43-44°	-75.5° (c 1.0 $CHCl_3$)	36
3-Deoxy-1,2-O-isopropylidene-3-thiocyanato-α-D-glucofuranose	syrup	-76.6° (c 1.0 $CHCl_3$)	36
3-Deoxy-1,2-O-isopropylidene-3-thiocyanato-5,6-di-O-acetyl-α-D-glucofuranose	syrup	-29.4° (c 1.0 $CHCl_3$)	36

ACKNOWLEDGMENT

We wish to thank Dr. James R. Daniel, Department of Food and Nutrition, Purdue University, West Lafayette, Indiana, 47907, U. S. A. for helpful discussion and reading this manuscript.

REFERENCES

1. E. Fischer, Chem. Ber., 1914, 47, 1377.
2. A. Müller and A. Wilhelms, Chem. Ber., 1941, 74, 698.
3. P. Walden and L. F. Audrieth, Chem. Rev., 1928, 5, 339.
4. N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, J. Am. Chem. Soc., 1955, 77, 6269.
5. E. L. Wagner, J. Chem. Phys., 1965, 43, 2728.
6. W. J. Le Noble, Synthesis, 1970, 1, 1.
7. A. Fava, A. Jliceto and S. Bresadola, J. Am. Chem. Soc., 1965, 87, 4791.
8. G. L. Caldow and H. W. Thompson, Spectrochim. Acta, 1958, 13, 212: E. Lieber, C. N. R. Rao and J. Ramachandran, Spectrochim. Acta, 1959, 13, 296.
9. A. Mathias, Tetrahedron, 1965, 21, 1073.
10. L. A. Spurlock, R. K. Porter and W. G. Cox, J. Org. Chem., 1972, 37, 1162.
11. E. Fischer, B. Helferich and P. Ostmann, Chem. Ber., 1920, 53, 884.
12. J. Stanek and L. Tajmr, Chem. Listy, 1958, 52, 551. Chem. Abstr., 53, 4146, 1959.
13. J. Stanek and L Tajmr, Coll. Czechoslov. Chem. Comm., 1958, 24, 1013.
14. a) A. C. Richardson, Carbohydr. Res., 1969, 10, 395; b) D. H. Ball and F. W. Parrish, Advan. Carbohydr. Chem. Biochem., 1968, 23, 233; ibid., 1969, 24, 139.
15. J. C. P. Schwarz and K. C. Yule, Proc. Chem. Soc., 1961, 417.
16. J. Hill, L. Hough and A. C. Richardson, Proc. Chem. Soc., 1963, 346.
17. K. Tokuyama, Bull. Chem. Soc. Japan, 1964, 37, 1133.
18. K. Tokuyama, M. Kiyokawa and M. Katsuhara, J. Org. Chem., 1965, 30, 4057.
19. J. Defaye and J. Hildesheim, Carbohydr. Res., 1970, 4, 145.
20. A. F. Cook and W. G. Overend, J. Chem. Soc. (C), 1966, 1549.
21. L. N. Owen and P. L. Ragg, J. Chem. Soc. (C), 1966, 1291.
22. S. D. Gero, Tetrahedron Lett., 1966, 3193; S. D. Gero and R. D. Guthrie, J. Chem. Soc. (C), 1967, 1761.
23. N. K. Kochetkow, E. J. Budovskii, V. N. Shibaev, and Yu. Yu. Kusov, Izv. Akad. Nauk. SSRR, Ser. Chim., 1970, 350.
24. N. K. Kochetokow, V. N. Shibaev, Yu. Yu. Kusov and M. F. Traitski, Izv. Akad. Nauk. SSRR, Ser. Chim., 1973, 425.

25. L. Vegh and E. Hardegger, Helv. Chim. Acta, 1973, 56, 1792.

26. J. Hill, L. Hough and A. C. Richardson, Carbohydr. Res., 1968, 8, 19.

27. R. J. Ferrier and N. Vethaviyasar, Chem. Comm., 1970, 1385.

28. R. J. Ferrier and N. Vethaviyasar, J. Chem. Soc. (C), 1971, 1907.

29. R. D. Guthrie and G. J. Williams, Chem. Comm., 1971, 923.

30. D. M. C. Hull, P. F. Orchard and L. N. Owen, J. Chem. Soc. Perkin Tr. I., 1977, 1234.

31. B. Gross and F. X. Oriez, Carbohydr. Res., 1974, 36, 385.

32. R. A. Boigegrain and B. Gross, Carbohydr. Res., 1975, 41, 135.

33. W. E. Dennis, Ph.D. Thesis, Wayne State University, 1966.

34. J. P. Dickerson, Ph.D. Thesis, Wayne State University, 1966.

35. L. A. Reed III and L. Goodman, Carbohydr. Res., 1981, 94, 91.

36. P. A. Risbood, T. S. Philips and L. Goodman, Carbohydr. Res., 1981, 94, 101.

37. Z. J. Witczak, manuscript in preparation.

38. R. W. Binkley and D. G. Hehemann, J. Org. Chem., 1978, 43, 3244.

39. R. W. Binkley, M. G. Ambrose and D. G. Hehemann, J. Org. Chem., 1980, 45, 4387.

40. R. W. Binkley, H. F. Jarrell, J. Carbohydr. Nucleosides Nucleotides, 1980, 7, 347.

41. M. G. Ambrose and R. W. Binkley, J. Org. Chem., 1983, 48, 674.

Received, 18th April, 1983