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AN APPROACH TO A NEW CLASS OF SELENOSUGARS

A CONVENIENT SYNTHESIS OF GLYCOSYL ISOSELENOCYANATES

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Abstract—A new class of selenosugars—glycosyl isoselenocyanates—has been prepared via reaction of the corresponding glycosyl isocyanides with elemental Se under the catalytic influence of triethylamine. 2,3,4,5,6-Penta-O-acetyl-D-gluconyl isoselenocyanate was also prepared in moderate yield by reaction of 2,3,4,5,6-penta-O-acetyl-D-gluconyl chloride with potassium selenocyanate in anhydrous acetone. The isoselenocyanate structure is ascertained by physical (^{13}C-NMR, IR) and chemical methods—formation of selenoureas, and radical induced fragmentation by reaction with tri-n-butyltin hydride via intermediate isocyanide, to 1,5-anhydro-D-hexitols.

Growing interest in using various organoselenium derivatives[1] in organic synthesis inspired new developments in modern synthetic carbohydrate chemistry.[2] These developments call for efficient selective methodology for the formation of organoselenium intermediates as good precursors for the synthesis of wide groups of sugars,[3] selenosugars[4] and selenonucleoside analogs.[5]

Although a number of synthetic approaches to the above group of derivatives have been developed, there are few methods that appear to have versatility for construction of a variety of heterocyclic systems containing selenium.[6] Among these are approaches that involve alkylation of potassium selenocyanate as a source of Se for an organic molecule. While the application of the selenocyanate anion in organoselenium chemistry[7] is well known, in carbohydrate chemistry only a few examples of selenocyanates as an organoselenium intermediate are described.[8] So far as is known the isomeric monosaccharide isoselenocyanates have not yet been prepared. Among the methods of synthesis of alkyl and aryl isoselenocyanates that have been reported are, alkylation of the selenocyanate ion,[9] reaction of isocyanides with elemental Se,[10] reaction of N-arylcarbimidic dichlorides with selenide ion,[11] treatment of isocyanides with phosphorus(V) selenide,[12] and reaction of primary amines and carbon diselenide in the presence of mercury(II) chloride.[13]

Nucleophilic attack of the ambient pseudohalide selenocyanate ion on alkyl halides leads to selenocyanates or isoselenocyanates. Principally, however, only selenocyanates are formed in alkylation reactions owing to attack by the strongly nucleophilic Se atom on the respective substrates. Similarly S_N2 nucleophilic displacement of primary *p*-toluenesulfonyl group in carbohydrate tosylates[8] leads only to the formation of selenocyanates. In contrast, isomeric isoselenocyanates can be obtained only by the methods mentioned previously,[9-13] and in poor yield by thermal isomerization of selenocyanates.[14]

Among these methods, using various starting materials, only the reaction of isocyanides with elemental selenium is well suited for general use and large-scale preparation of isoselenocyanates.[7] Alkyl and aryl isoselenocyanates are important precursors for a number of organoselenium compounds such as selenoureas and selenosemicarbazides,[6] which also easily cyclize or transform to selenazole heterocycles. The fact that a selenazolenucleoside analog[15] has recently been found to be a good antitumor agent encouraged investigation of the introduction of Se into the sugar moiety at the anomeric position.

Glycosyl isocyanides, which are suitable precursors for the synthesis of corresponding isoselenocyanates, are known in carbohydrate literature,[16,17] and two methods of their synthesis are generally employed. The first of these methods involves the nucleophilic attack of ambident cyanide ion (silver cyanide) on glycosyl halides;[16,17] whereas the second is dehydration of the corresponding N-formylglucopyranosylamines.[18] The aforementioned methods and the chemistry of monosaccharide isocyanides have been reviewed.[19]

RESULTS AND DISCUSSION

Synthesis of 1-*isoselenocyano sugars*

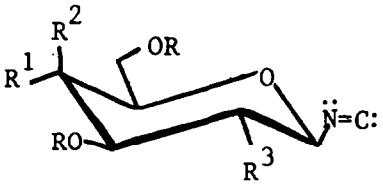
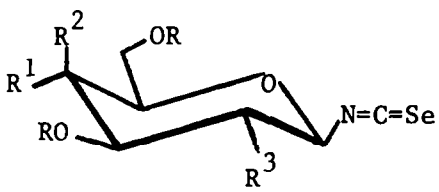
Glycosyl isocyanides **1–3** prepared according to the literature method[16,17,20] react with elemental Se under the conditions described by Sonoda *et al.*[21] to give the corresponding isoselenocyanates **4–6** in moderate yield. The yield of this reaction, however, is dependent on the solvent used and on the catalytic effect of triethylamine.[21]

In polar solvents such as tetrahydrofuran, the reaction occurs about four times as fast as in chloroform, which was also recommended as a solvent for the reaction of alkyl isocyanides with elemental Se.[10b] The best results obtained in chloroform and tetrahydrofuran are recorded in Table 1. However, these isoselenocyanates are air-sensitive compounds and unstable, gradually decomposed at room temperature. Attempts to deacetylate isoselenocyanates **4–6** were unsuccessful. Under strongly basic conditions, decomposition of starting materials with precipitation of metallic Se was observed. The physicochemical data of isoselenocyanates **4–6** are summarized in Table 2.

Identification of 1-*isoselenocyano sugars*

Spectroscopic methods. Spectrometric differences between selenocyanates and isoselenocyanates occur in

Table 1. Synthesis of glycosyl isoselenocyanates starting from glycosyl isocyanides

Starting material	Time of reaction (hr) and yields in $CHCl_3$		in THF		Products
					
1 $R = R^1 = R^3 = OAc, R^2 = H$	24	(51%)	4	(65%)	2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl isoselenocyanate (**4**)
2 $R = R^2 = R^3 = OAc, R^1 = H$	18	(42%)	3	(60%)	2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl isoselenocyanate (**5**)
3 $R = R^1 = OAc, R^2 = H, R^3 = NHAc$	12	(30%)	6	(48%)	2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl isoselenocyanate (**6**)

the stretching frequencies of the —Se—C≡N band in IR spectroscopy and in the chemical shifts of the carbon of the functional group in ^{13}C-NMR. The ^{13}C-NMR chemical shifts for the carbon of alkyl or aryl selenocyanates[22–25] appear at 101.9[22] and 109–129 ppm,[23] respectively. However, to our knowledge, no information exists concerning the ^{13}C-NMR chemical shift of isomeric isoselenocyanates. Our observations indicate that the ^{13}C chemical shift of the isoselenocyanate carbon is of low intensity and appears in the range of 144.8–146.8 ppm. The ^{13}C-NMR data of isoselenocyanates are listed in Table 3.

The IR —N=C=Se stretching frequencies constitute the main spectroscopic difference between selenocyanates and isoselenocyanates;[26–30] they are approximately 2127–2152 cm^{-1} in aryl series.

The stretching signal of glycosyl isoselenocyanates **4–6** appear in the region 2115–2160 cm^{-1}. Data listed in Table 2 are in agreement with those reported in the aryl series.[9c]

Chemical transformations

Chemical proof confirms the isoselenocyanate structure of compounds **4–6**. Reaction of glycosyl isoselenocyanates **4–6** with aniline produces the corresponding N-tetra-O-acetylglycosyl-N′-phenylselenoureas **7–9** in good yield, which were fairly stable at room temperature, in contrast to starting materials. However, attempts to prepare free sugars by deacetylation under Zemplen conditions were unsuccessful and decomposition of the starting selenourea with precipitation of metallic Se was always observed. The physicochemical data of selenoureas **7–9** are summarized in Table 4.

Two isolated reports in the literature indicate that the isoselenocyanate moiety can be reduced to the corresponding hydrocarbon by tri-n-butyltin hydride.[31,32] This radical-induced fragmentation of the isoselenocyanato group in steroid derivatives proceeds via isocyanide intermediate as reported by Barton *et al.*[31,32]

Furthermore, it was confirmed that radical-induced fragmentation of the isoselenocyanato group by reaction with tri-n-butyltin hydride is very useful in the structure determination of synthesized isoselenocyanates. The reaction of glycosyl isoselenocyanates **4–6** with tri-n-butyltin hydride in refluxing benzene in the presence of a radical initiator (AIBN) according to the procedure of Barton *et al.*,[31,32] afforded the 1,5-anhydro-D-hexitols **10–12** in good yield. However, when the reaction was conducted at room temperature, formation of intermediate isocyanides **1–3** was also observed, however, in poor yield (Scheme 1). These observations confirm the isoselenocyanate structure of

Table 2. Physicochemical data of isoselenocyanates

Compound	R_f[a]	$[\alpha]_D^{20}$[b]	IR ν_{max} cm^{-1} (NCSe)[c]	Formula	Analytical data	Calc	Found
4	0.57	+4.8	2130	$C_{15}H_{19}NO_9Se$	C H N	41.29 4.38 3.21	40.89 4.11 3.11
5	0.44	−11.2	2160	$C_{15}H_{19}NO_9Se$	C H N	41.29 4.38 3.21	40.62 4.49 3.06
6	0.36	+10.8	2115	$C_{15}H_{20}N_2O_8Se$	C H N	41.38 4.63 6.43	40.98 4.77 6.28

[a]TLC solvent; benzene–ether–light petroleum (6:3:1).
[b]In $CHCl_3$.
[c]Film.

Table 3. ^{13}C-NMR data (δ) of isoselenocyanates[a]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	NCSe
4	91.8	70.5	72.8	68.1	72.8	61.7	146.2
5	91.8	67.8	70.6	66.8	71.5	61.0	146.6
6	96.2	58.3	75.1	71.2	77.2	62.0	144.8

[a]For solution in $CDCl_3$; signals downfield from signal of internal Me_4Si in $CDCl_3$.

compounds **4–6** and earlier results of Barton *et al.*[31,32] on the radical-induced fragmentation of isoselenocyanates.

Another class of isoselenocyanates, acyl isoselenocyanates,[37] is well known and their chemistry has been reviewed.[38,39] Takahashi *et al.*[37] synthesized the first monosaccharide acyl isothiocyanate, 2,3,4,5,6-penta-O-acetyl-D-gluconyl isothiocyanate, by action of silver thiocyanate on 2,3,4,5,6-penta-O-gluconyl chloride[40] (**13**) in dry xylene. However, the seleno counterpart, 2,3,4,5,6-penta-O-acetyl-D-gluconyl isoselenocyanate (**14**), has not yet been prepared. For the preparation of this compound the general procedure of synthesis for alkyl and aryl isoselenocyanates[41] was adopted. This synthetic approach proceeds from D-glucono-1,5-lactone via 2,3,4,5,6-penta-O-acetyl-D-gluconyl chloride[40] (**13**) which on reaction with potassium selenocyanate affords isoselenocyanate **14** in 62% yield. IR spectrum of **14** shows a characteristic absorption band for isoselenocyanates[10d] at 2130 cm^{-1} which easily differentiates it from selenocyanate. The ^{13}C-NMR spectrum of **14** exhibited a chemical shift at 146.8 ppm which is probably due to the carbon of N=C=Se group. Isoselenocyanate **14** is a highly unstable compound, easily decomposed at room temperature, and any attempt at synthesis of the free sugar from **14** by deacetylation under Zemplen conditions is unsuccessful. In contrast N-2,3,4,5,6-penta-O-acetyl-D-gluconyl-N′-phenylselenourea (**15**) prepared from **14** is a stable crystalline compound.

EXPERIMENTAL

All m.ps were determined with a Fisher–Johns apparatus and were not corrected. Optical rotations were measured with a Perkin–Elmer Model 141 polarimeter. IR spectra were recorded with a Perkin–Elmer IR-177 spectrophotometer. ^{13}C-NMR spectra were recorded at 50.3 MHz for solution in $CDCl_3$ (internal standard Me_4Si) with a Nicolet NT-200 NMR spectrometer. The purity of products was determined by TLC on silica gel plates GF_{254} (Merck), and the components were detected by spraying with 5% H_2SO_4 in EtOH and charring. The following chromatographic solvent systems were used (v/v) 7:2:1 EtOAc–CH_2Cl_2–MeOH (solvent A), benzene–ether–light petroleum 6:3:1 (solvent B). Flash chromatography was performed on silica gel (60–200 mesh) EM9385 Baker Analytical Reagents.[42]

All organic solvents were dried with Na_2SO_4 and evaporated (generally 40°) under reduced pressure. Starting isocyanides **1** and **2** were prepared according to the method of Martin-Lomas and Chacon-Fuertes;[16] whereas isocyanide **3** by desulfurization of corresponding isothiocyanate with tri-n-butyltin hydride.[20] Microanalyses were performed in the Chemistry Department, Purdue University.

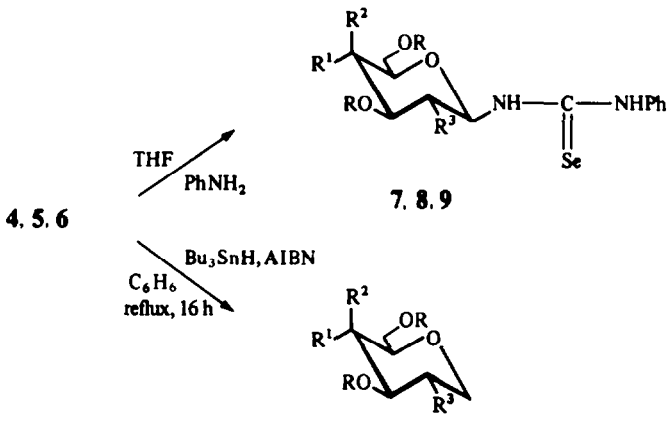
Glycosyl isoselenocyanates **4–6**

General procedure. To the soln of **1–3** 1.4 g (4 mmol) in 30 ml of dry $CHCl_3$ or THF were added 0.32 g (4 mmol) of elemental Se and 1 ml of Et_3N. The mixture was kept in the dark and stirred and heated under reflux temp for the time indicated in Table 1. After completion of reaction (monitored by TLC solvent B) the mixture was filtered and evaporated to a syrup. The syrupy products were finally purified by faster flash-column chromatography (elution with solvent B) collecting fractions containing R_f indicated in Table 1.

Table 4. Physiochemical data of N′-phenylselenoureas

Compound	Yield (%)	M.p. (°)	IR ν_{max} cm^{-1} (NH)	Formula Analytical data Calc	Found
N-2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl-N′-phenylselenourea (**7**)	88	81–83[a]	3220	$C_{21}H_{26}N_2O_9Se$ (529.4)	
				C, 47.64	47.31
				H, 4.95	4.63
				N, 5.29	5.06
N-2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl-N′-phenylselenourea (**8**)	76	syrup	3210[b]	$C_{21}H_{26}N_2O_9Se$ (529.4)	
				C, 47.64	47.26
				H, 4.95	4.92
				N, 5.29	5.12
N-2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl-N′-phenylselenourea (**9**)	62	syrup	3200[b] 3210	$C_{21}H_{27}N_3O_8Se$ (528.4)	
				C, 47.72	47.43
				H, 5.15	4.92
				N, 7.95	7.61

[a]Crystallized from benzene.
[b]Film.



Scheme 1.

Glycosyl selenoureas **7–9**

General procedure. To a soln of **4–6** 0.8 g (2 mmol) in 20 ml of THF was added dropwise a soln of 0.18 g (2 mmol) of aniline. After completion of amine, the mixture was stirred and heated under reflux temp for 2 h to complete the reaction, which was monitored by TLC (solvent A). The soln was evaporated to a syrup, and crystallized from benzene.

2,3,4,6-*Tetra-acetyl*-1,5-*anhydro*-D-*hexitols* **10–12**

General procedure. To a boiling and magnetically stirred soln of isoselenocyanates **4–6** 0.6 g (2 mmol) in benzene (50 ml) containing 0.05 g of AIBN (azobisisobutyronitrile) was added dropwise a soln of 0.6 g (2 mmol) of tri-n-butyltin hydride. The mixture was stirred and heated under reflux temp (N_2 atmosphere) for 16 h, monitoring the progress of reaction by TLC (solvent A). After completion of reaction to the cooled mixture a soln of KF[34] 3.5 g in 30 ml of water was added and the mixture was stirred for 30 min. The ppt was filtered off. The water was separated from the filtrate and the benzene layer was dried and evaporated to the syrup, which was crystallized from ether–light petroleum or EtOH.

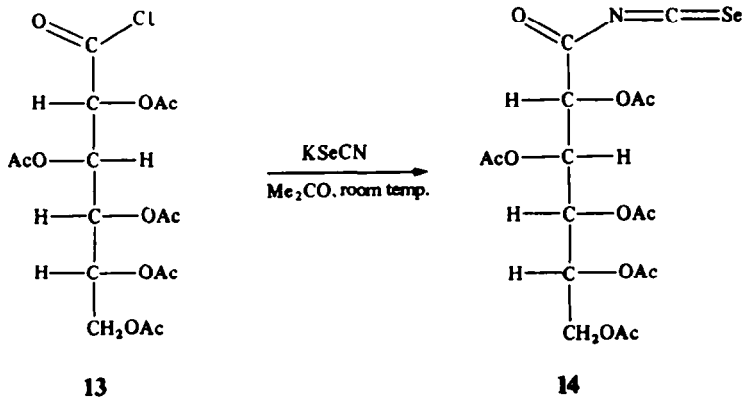
2,3,4,6 - *Tetra* - O - *acetyl* - 1,5 - *anhydro* - D - *glucitol* (**10**). Prepared from **4**, yield 76%, m.p. 72–74° (ether–light petroleum), $[\alpha]_D^{20}$ +42°; lit.[33,34] m.p. 71–73°, $[\alpha]_D^{20}$ +42.7°.

2-*Acetamido* - 3,4,6 - *tri* - O - *acetyl* - 1,5 - *anhydro* - 2 - *deoxy* - D - *glucitol* (**12**). Prepared from **6**, yield 81%, m.p. 164–166°, $[\alpha]_D^{20}$ 0°; lit.[36] m.p. 165–168°.

2,3,4,5,6-*Penta*-O-*acetyl*-D-*gluconyl isoselenocyanate* (**14**). To a stirred soln of 5.0 g (34 mmol) of potassium selenocyanate in 150 ml of anhyd acetone, 14.7 g (34 mmol) of **13**[40] in 30 ml of anhyd acetone was added in portion during 30 min. The mixture was stirred at room temp for 2 h, the ppt of KCl was filtered off, and the filtrate was concentrated under reduced pressure to the syrup. Yield 10.65 g (62%), of homogeneous product on TLC (solvent A), R_f = 0.61, $[\alpha]_D^{20}$ +54° (c 0.5 $CHCl_3$), IR max cm^{-1} 2130; ^{13}C-NMR 170.6 (OAc), 170.2, 169.4 (double intensity), 167.8 (C=O), 146.8 (NCSe weak), 71.0 (C-2), 70.4 (C-3), 70.2 (C-4), 67.7 (C-5), 61.7 (C-6), 22.1 (OAc), 20.7 (double intensity, OAc). (Found: C, 40.96; H, 4.04; N, 2.61. Calc for $C_{17}H_{21}NO_{11}Se$ (494.30): C, 41.30; H, 4.28; N, 2.83%.)

N - 2,3,4,5,6 - *Penta* - O - *acetyl* - D - *gluconyl* - N' - *phenylselenourea* (**15**)

To a soln of 2.47 g (5 mmol) of **14** in 20 ml of dry THF was added dropwise 0.46 g (5 mmol) of aniline. After addition of amine, the mixture was stirred and heated at reflux temp for 2 hr to complete the reaction. The mixture was evaporated under reduced pressure to a syrup. Flash chromatography of the crude product on silica gel column by elution with solvent B gave **15** as a chromatographically homogeneous syrup (R_f = 0.42). Crystallization from benzene gave crystalline **15** (yield 2.37 g, 81%), m.p. 89–92°, $[\alpha]_D^{20}$ + 56.8° (c 0.5 $CHCl_3$); IR ν_{max}^{KBr} cm^{-1} 1750 (C=O), 3220 (NH) cm^{-1}. (Found: C, 46.83; H, 4.61; N, 4.52. Calc for $C_{23}H_{28}N_2O_{11}Se$ (587.44): C, 47.02; H, 4.80; N, 4.76%.)



Scheme 2.

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REFERENCES

[1] For recent reviews on organoselenium chemistry and organoselenium reagents see; D. L. J. Clive, *Tetrahedron* **34**, 1049 (1978); H. J. Reich, *Acc. Chem. Res.* **12**, 22 (1979); H. J. Reich, *Oxidation in Organic Chemistry* (Edited by W. Trahanovsky), Part C, 1. Academic Press, New York (1978); D. Liotta, *Acc. Chem. Res.* **17**, 28 (1984); L. Syper and J. Młochowski, *Synthesis* 439 (1984).

[2] For recent examples on organoselenium intermediates in carbohydrate chemistry; S. Current and K. B. Sharpless, *Tetrahedron Lett.* 5075 (1978); A. P. Kozikowski, K. L. Sorgi and R. J. Schmiesing, *J. Chem. Soc. Chem. Commum.* 477 (1980); K. Furnichi, S. Yogai and T. Miwa, *Ibid. Chem. Commun.* 66 (1980); A. G. M. Barret, R. W. Read and D. H. R. Barton, *Ibid. Perkin Trans. 1* 2184 (1980); G. Jaurand, J. M. Beau and P. Sinäy, *Ibid. Chem. Commun.* 572 (1981); P. Rollin, V. Verez Bencomo and P. Sinäy, *Synthesis* 134 (1984).

[3] Y. Nishimura, H. Umezawa and S. Umezawa, *Tetrahedron Lett.* 77 (1981); H. Paulsen, F. R. Heiker, J. Feldmann and K. Heyns, *Synthesis* 636 (1980); W. Kudelska and M. Michalska, *Tetrahedron* **37**, 2994 (1981).

[4] For recent review on selenosugars see; Z. J. Witczak and R. L. Whistler, *Heterocycles* **19**, 1719 (1982).

[5] For recent review on synthesis and chemistry of selenonucleosides see; Z. J. Witczak, *Nucleosides Nucleotides* **2**, 295 (1983).

[6] E. Bulka, *Organic Selenium Compounds* (Edited by D. L. Klayman and W. M. H. Günther), p. 459. Wiley, New York (1973).

[7] E. Bulka, *The Chemistry of Cyanates and their Thio Derivatives* (Edited by S. Patai), p. 887. Wiley-Interscience, New York (1977).

[8] T. Van Es, *Carbohydr. Res.* **5**, 282 (1967); T. Van Es and R. L. Whistler, *Tetrahedron* **23**, 2849 (1971); J. J. Rabelo and T. Van Es, *Carbohydr. Res.* **30**, 381 (1973); J. R. Daniel and R. A. Zingaro, *Carbohydr. Res.* **64**, 69 (1978).

[9] C. T. Pedersen, *Acta Chem. Scand.* **17**, 1459 (1963).

[10a] K. A. Jensen and E. Fredriksen, *Z. Anorg. Allgem. Chem.* **230**, 31 (1936); [b] M. Lipp, F. Dallacker and I. M. zu Kocker, *Monatsh. Chem.* **90**, 41 (1959); [c] W. J. Franklin and R. L. Werner, *Tetrahedron Lett.* 3003 (1965); [d] E. Bulka, K. D. Ahlers and E. Tućek, *Chem. Ber.* **100**, 1369 (1967).

[11] H. Stolle, *Ber. Dtsch. Chem. Ges.* **19**, 2350 (1886).

[12] C. Collard-Charon and M. Renson, *Bull. Soc. Chim. Belg.* **71**, 531 (1962).

[13] L. Henriksen and U. Ehrbar, *Synthesis* 519 (1976).

[14] A. Fava, *Organic Sulfur Compounds* (Edited by N. Kharasch and C. Y. Meyers), Vol. 2, p. 73. Pergamon Press, New York (1966).

[15] P. Srivastava and R. K. Robins, *J. Med. Chem.* **26**, 445 (1983).

[16] M. Martin-Lomas and M. E. Chacon-Fuertes, *Carbohydr. Res.* **59**, 604 (1977).

[17] P. Boullanger and G. Descotes, *Tetrahedron Lett.* 3427 (1976); P. Boullanger, D. Marmet and G. Descotes, *Tetrahedron* **35**, 163 (1979).

[18] R. J. M. Nolte, J. A. J. Van Zomeren and J. W. Zwikker, *J. Org. Chem.* **43**, 1972 (1978).

[19] Z. J. Witczak, *J. Carbohydr. Chem.* **3**, 359 (1984).

[20] Z. J. Witczak, Unpublished results.

[21] N. Sonoda, G. Yamamoto and S. Tsutsumi, *Bull. Chem. Soc. Japan* **45**, 2937 (1972).

[22] G. A. Kalabin, D. F. Kushnarev, G. A. Chmutova and L. V. Kashurnikova, *Zh. Org. Khim.* **15**, 19 (1979).

[23] J. A. Kargol, R. W. Crecely and J. L. Burmeister, *Inorg. Chem.* **18**, 2532 (1979).

[24] G. Llabres, M. Baiwir, J. L. Piette and L. Christiaenes, *Org. Magn. Reson.* **15**, 152 (1981).

[25] L. Christiaens and J. L. Piette, *Org. Magn. Reson.* **21**, 461 (1983).

[26] D. Martin and W. M. Brause, *J. Prakt. Chem.* **312**, 789 (1970).

[27] D. Martin, W. M. Brause and R. Radeglia, *J. Prakt. Chem.* **312**, 797 (1970).

[28] D. Martin and W. M. Brause, *J. Prakt. Chem.* **312**, 812 (1970).

[29] S. Stankovsky and S. Kovac, *Tetrahedron* **29**, 4175 (1973).

[30] W. J. Franklin, R. L. Werner and R. A. Ashby, *Spectrochim. Acta* **30A**, 1293 (1974).

[31] D. H. R. Barton, G. Bringmann, G. Lamotte, R. S. H. Motherwell and W. B. Motherwell, *Tetrahedron Lett.* 2291 (1979).

[32] D. H. R. Barton, G. Bringmann, G. Lamotte, R. S. H. Motherwell, W. B. Motherwell and A. E. A. Porter, *J. Chem. Soc. Perkin Trans. 1* 2665 (1980).

[33] J. Auge and S. David, *Carbohydr. Res.* **59**, 225 (1977).

[34] P. Kocienski and C. Pant, *Ibid.* **110**, 330 (1982).

[35] E. J. Hedgley and H. G. Fletcher, *J. Am. Chem. Soc.* **85**, 1615 (1963).

[36] D. Horton and M. L. Wolfrom, *J. Org. Chem.* **27**, 1794 (1962).

[37] H. Takahashi, K. Takeda, N. Nimura and H. Ogura, *Chem. Pharm. Bull.* **27**, 1137 (1979).

[38] R. Esmail and F. Kurzer, *Synthesis* 301 (1975).

[39] M. O. Lozinskii and P. S. Pelkis, *Russian Chem. Rev.* **37**, 363 (1968).

[40] R. T. Major and E. W. Cook, *J. Am. Chem. Soc.* **58**, 2477 (1936); *Ibid.* **58**, 2477 (1936).

[41] B. I. Douglas, *J. Am. Chem. Soc.* **59**, 740 (1937).

[42] W. C. Still, M. Khan and A. Mitra, *J. Org. Chem.* **43**, 2923 (1978).