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Circular Dichroism of Acetylated Methyl Glycosides. Part II*

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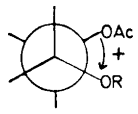
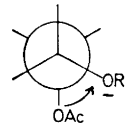
The CD spectra, in ethanol, of twentytwo methyl-D-hexopyranoside acetates with the *O*-acetyl groups in the 4-, 6-, 2,3-, 2,6-, 3,4-, 3,6-, and 4,6-positions have been recorded. Possible relationships between the observed Cotton effects and the molecular geometry of the acetoxy groups and neighbouring oxygen atoms are discussed.

In a previous paper the circular dichroism of the 2-*O*-acetyl and 3-*O*-acetyl derivatives of the methyl D-hexopyranosides of D-galactose, D-glucose and D-mannose were recorded.[1] The signs of the observed Cotton effects were empirically correlated with the dihedral angle between the acetoxy group and a vicinal oxygen atom. Thus (1) was considered to give rise to a positive Cotton effect and (2) correspondingly a negative one.



(1)



(2)

Arrangements with the acetoxy group and the vicinal oxygen in a *trans* relationship were considered to give no Cotton effect. Furthermore, it was found necessary to postulate that the contribution to the circular dichroism for R = H in (1) and (2) exceeded that for R = CH_3. Contributions from vicinal carbon (and hydrogen) atoms were neglected. Also, the orientation of the chromophore may be different in the substances studied. It is possibly for these reasons that correlations of molecular geometry with the signs, but not with the magnitudes of the observed CD could be obtained. In the present paper these studies have been extended to methyl D-hexopyranosides with the *O*-acetyl groups in the 4 and 6-positions, and to some di-*O*-acetyl derivatives.

* Part I, Ref. 1.

The various acetates were synthesized by conventional routes. The 4-acetates of methyl α-D-glucopyranoside, methyl β-D-glucopyranoside, methyl α-D-galactopyranoside, methyl β-D-galactopyranoside, and methyl α-D-mannopyranoside were prepared, starting from the appropriate methyl 4,6-*O*-benzylidene hexopyranosides. These were benzylated in the 2,3-positions. The benzylidene groups were removed by mild acid hydrolysis. The primary hydroxyls in the 6-positions were tritylated (glucosides and mannosides) or benzylated (galactosides) and the remaining hydroxyl groups in the 4-positions acetylated. Catalytic hydrogenation removed trityl and benzyl groups and afforded the 4-acetates. The 6-*O*-acetyl derivatives of the same methyl hexopyranosides were obtained from the above methyl 2,3-di-*O*-benzylhexopyranosides by partial acetylation and obtained in pure form by silica gel chromatography.

Table 1. Positions and amplitudes of CD maxima of some hexoside acetates.

Substance	Ref. [a]	CD maximum (nm)	θ (°)	Predicted sign for θ
Methyl 3-*O*-acetyl-2-*O*-methyl-α-D-glucopyranoside		nil		+
Methyl-4-*O*-acetyl-α-D-glucopyranoside		213	−725	−
Methyl-4-*O*-acetyl-β-D-glucopyranoside		212	−489	−
Methyl-4-*O*-acetyl-β-D-galactopyranoside		218	+174	+
Methyl-4-*O*-acetyl-α-D-mannopyranoside		214	−1650	−
Methyl-6-*O*-acetyl-α-D-glucopyranoside	8	234	+218	+
		217	−348	−
Methyl-6-*O*-acetyl-β-D-glucopyranoside	9	214	−286	−
Methyl-6-*O*-acetyl-α-D-galactopyranoside		217	−212	−
Methyl-6-*O*-acetyl-β-D-galactopyranoside	2	217	−180	−
Methyl 6-*O*-acetyl-α-D-mannopyranoside		242	+226	+
		217	−552	−
Methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside	10	218	−835	−
Methyl 2,3-di-*O*-acetyl-β-D-glucopyranoside	11	217	+558	+
Methyl 2,3-di-*O*-acetyl-α-D-galactopyranoside	12	217	−3180	−
Methyl 2,3-di-*O*-acetyl-β-D-galactopyranoside	12	217	−2410	−
Methyl 2,3-di-*O*-acetyl-β-D-mannopyranoside	13	214	+1055	+
Methyl 2,6-di-*O*-acetyl-β-D-galactopyranoside		218	+101	−
		228	−81	−
Methyl 3,4-di-*O*-acetyl-β-D-galactopyranoside		215	−745	−
Methyl 3,6-di-*O*-acetyl-α-D-galactopyranoside		216	−1620	−
Methyl 4,6-di-*O*-acetyl-α-D-glucopyranoside		239	+600	+
		217	−1050	−
Methyl 4,6-di-*O*-acetyl-α-D-galactopyranoside		213	+864	+
Methyl 4,6-di-*O*-acetyl-β-D-galactopyranoside		213	+1120	+
Methyl 4,6-di-*O*-acetyl-α-D-mannopyranoside		211	−2210	−
		237	−2320	

[a] For new compounds see Table 2.

Table 2. New compounds.

Compound	Synthetic precursor	Method of synthesis	Yield from precursor (%)
Methyl 4-*O*-acetyl-2,3-di-*O*-benzyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (I)	Methyl 2,3-di-*O*-benzyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (II)[14]	*a*	90
Methyl 4-*O*-acetyl-α-D-glucopyranoside	I	*b*	100
Methyl 4-*O*-acetyl-2,3-di-*O*-benzyl-6-*O*-triphenylmethyl-β-D-glucopyranoside (III)	Methyl 2,3-di-*O*-benzyl-6-*O*-triphenylmethyl-β-D-glucopyranoside (IV)[15]	*a*	90
Methyl 4-*O*-acetyl-β-D-glucopyranoside	III	*b*	100
Methyl 2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (IV)	Methyl 2,3-di-*O*-benzyl-β-D-galactopyranoside (V)[16]	*c*	35
Methyl 4-*O*-acetyl-2,3,6-tri-*O*-benzyl-β-D-galactopyranoside (VI)	IV	*a*	76
Methyl 4-*O*-acetyl-β-D-galactopyranoside	VI	*b*	100
Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (VII)	Methyl 4,6-*O*-benzylidene-α-D-mannopyranoside (VIII)[17]	*d*	68
Methyl 2,3-di-*O*-benzyl-α-D-mannopyranoside (IX)	VIII	*e*	52
Methyl 2,3-di-*O*-benzyl-6-*O*-triphenylmethyl-α-D-mannopyranoside (X)	IX	*f*	66
Methyl 4-*O*-acetyl-2,3-di-*O*-benzyl-6-*O*-triphenylmethyl-α-D-mannopyranoside (XI)	X	*a*	88
Methyl 4-*O*-acetyl-α-D-mannopyranoside	XI	*b*	100
Methyl 6-*O*-acetyl-2,3-di-*O*-benzyl-α-D-glucopyranoside	Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside (XII)[18]	*g*	60
Methyl 6-*O*-acetyl-2,3-di-*O*-benzyl-β-D-glucopyranoside	Methyl 2,3-di-*O*-benzyl-β-D--glucopyranoside (XIII)[19]	*g*	58
Methyl 6-*O*-acetyl-2,3-di-*O*-benzyl-α-D-galactopyranoside	Methyl 2,3-di-*O*-benzyl-α-D-galactopyranoside (XIV)[20]	*g*	72
Methyl 6-*O*-acetyl-α-D-galactopyranoside	XIV	*b*	100
Methyl 6-*O*-acetyl-2,3-di-*O*-benzyl-α-D-mannopyranoside (XV)	IX	*g*	55
Methyl 6-*O*-acetyl-β-D-mannopyranoside	XV	*b*	100
Methyl 2,6-di-*O*-acetyl-β-D-galactopyranoside	Methyl 2,6-di-*O*-acetyl-3,4-*O* benzylidene-β-D-galactopyranoside [2]	*b*	86
Methyl 2,6-di-*O*-benzyl-β-D-galactopyranoside (XVI)	Methyl 3,4-*O*-benzylidene-β-D-galactopyranoside [2]	*h*	65
Methyl 3,4-di-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (XVII)	XVI	*a*	70
Methyl 3,4-di-*O*-acetyl-β-D-galactopyranoside	XVII	*b*	100
Methyl 4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-α-D-glucopyranoside (XVIII)	XII	*a*	100
Methyl 4,6-di-*O*-acetyl-α-D-glucopyranoside	XVIII	*b*	100
Methyl 4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (XIX)	XIV	*a*	100
Methyl 4,6-di-*O*-acetyl-α-D-galactopyranoside	XIX	*b*	100
Methyl 4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-β-D-galactopyranoside (XX)	V	*a*	90
Methyl 4,6-di-*O*-acetyl-β-D-galactopyranoside	XX	*b*	100
Methyl 4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-α-D-mannopyranoside (XXI)	IX	*a*	100
Methyl 4,6-di-*O*-acetyl-α-D-mannopyranoside	XXI	*b*	100
Methyl 3-*O*-acetyl-2-*O*-methyl-α-D-glucopyranoside	Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-methyl-α-D-glucopyranoside [21]		100

Solvent for TLC Purification	Solvent for crystallization	$[\alpha]_D$ (°)	Solvent for rotation	m.p. (°)	Analysis C	Analysis H %	Required analysis C	Required analysis H %
$CHCl_3$ – Et_2O 9:1	MeOH – EtOAc	+23	$CHCl_3$	134 – 7	76.7	6.51	76.6	6.43
–	–	+119	H_2O	–				
$CHCl_3$ – Et_2O 9:1	MeOH – EtOAc	+5	$CHCl_3$	158 – 161	76.8	6.57	76.6	6.43
–	–	−20	H_2O	119 – 126	45.6	6.57	45.8	6.83
Light petr. [j] – EtOAc 2:1	–	+3	$CHCl_3$	–				
Light petr. [j] – EtOAc 3:1	–	+20	$CHCl_3$	–				
–		−4	EtOH					
Light petr. [j] – EtOAc 4:1	–	+25	$CHCl_3$	–	72.7	6.59	72.7	6.54
$PhCH_3$ – EtOAc 4:1	–	−2	$CHCl_3$	–	67.2	6.81	67.4	7.00
$PhCH_3$ – EtOAc 4:1	–	−9	$CHCl_3$	–	77.9	6.64	77.9	6.54
$CHCl_3$ – Et_2O 9:1	–	−5	$CHCl_3$	–	76.8	6.33	76.6	6.43
–	–	+55	H_2O	–				
$CHCl_3$ – Me_2CO 8:1	–	+18	$CHCl_3$	–	66.3	6.93	66.3	6.78
$CHCl_3$ – Me_2CO 5:1	–	−20	$CHCl_3$	–	66.5	6.80	66.3	6.78
Light petr. [j] – EtOAc 2:1	MeOH	+13	$CHCl_3$	139 – 141	66.9	7.09	66.3	6.78
–	Me_2CO	+160	EtOH	154 – 6	45.9	6.68	45.8	6.83
$CHCl_3$ – Me_2CO 85:15	–	−9	$CHCl_3$	–	66.2	6.75	66.3	6.78
–	–	+67	EtOH	–				
–	Et_2O	−12	$CHCl_3$	105 – 111	47.3	6.40	47.5	6.52
$CHCl_3$ – Et_2O 7:3	Et_2O light petr.	+10	$CHCl_3$	79 – 80	67.1	7.16	67.4	7.00
$CHCl_3$ – Et_2O 8:2	–	+14	$CHCl_3$	–	65.5	6.43	65.5	6.60
–	–	+32	$CHCl_3$	–	–	–		–
–	–	+13	$CHCl_3$	–	65.6	6.72	65.5	6.60
–	–	+96	$CHCl_3$	–	–	–	–	–
Light petr. [j] – EtOAc 2:1	–	+52	$CHCl_3$	–	–	–	–	–
–	–	+111	EtOH	–	–	–	–	–
Light petr. [j] – EtOAc 2:1	Pr^i_2O	+28	$CHCl_3$	108 – 9	65.7	6.97	65.5	6.60
–	Pr^i_2O	−1	EtOH	109 – 112	47.3	6.5	47.5	6.52
–	–	−5	$CHCl_3$	–	65.7	6.64	65.5	6.60
–	–	+38	$CHCl_3$	–	–	–	–	–
–	Pri_2O	+150	EtOH	84 – 6	47.9	7.30	48.0	7.25

[a] Ac_2O, C_5H_5N. [b] Pd/H_2. [c] 1 mol equiv. $PhCH_2Br$, Ag_2O, DMF. [d] $PhCH_2Br$, Ag_2O, DMF. [e] 90 % aq. CF_3COOH. [f] Ph_3CCl, C_5H_5N. [g] 1 mol equiv. Ac_2O, C_5H_5N. [h] $PhCH_2Br$, NaH, DMF. [j] 40 – 60° throughout.

The 2,3-di-*O*-acetyl derivatives of methyl α-D-glucopyranoside, methyl β-D-glucopyranoside, methyl α-D-galactopyranoside, methyl β-D-galactopyranoside, and methyl α-D-mannopyranoside were obtained by acetylation of the appropriate methyl 4,6-*O*-benzylidene hexopyranosides followed by catalytic hydrogenation.

Methyl 2,6-di-*O*-acetyl-β-D-galactopyranoside was obtained from methyl 2,6-di-*O*-acetyl-3,4-*O*-benzylidene-β-D-galactopyranoside [2] by catalytic hydrogenation. Methyl 3,4-di-*O*-acetyl-β-D-galactopyranoside was obtained from methyl 3,4-*O*-benzylidene-β-D-galactopyranoside [2] by benzylating the 2- and 6-positions, removing the benzylidene group with mild acid, acetylating the free hydroxyl groups in the 3- and 4-positions and finally removing benzyl groups from the 2- and 6-positions by catalytic hydrogenation.

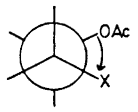
The 4,6-di-*O*-acetyl derivatives of methyl α-D-glucopyranoside, methyl α-D-galactopyranoside, methyl β-D-galactopyranoside, and methyl α-D-mannopyranoside were prepared from the appropriate methyl 2,3-di-*O*-benzyl-hexopyranosides described above, by acetylation followed by catalytic hydrogenation.

Methyl 3,6-di-*O*-acetyl-α-D-galactopyranoside was produced from the 4,6-acetate by spontaneous acetyl migration by standing as a syrup. Its constitution follows from NMR evidence.

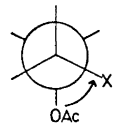
Methyl 3-*O*-acetyl-2-*O*-methyl-α-D-glucopyranoside was obtained by catalytic hydrogenation of the corresponding 4,6-*O*-benzylidene derivative.

Literature references for all known compounds are given in Table 1; the syntheses and pertinent data for all new compounds are summarized in Table 2.

Positions and amplitudes for the various CD maxima are given in Table 1. The results may be rationalized following the same argumentation as that previously presented. It is assumed that unit (3) gives a positive Cotton effect, while that of (4) gives a negative one.[1]



(3)



(4)

X = −O−, −OH, −OMe, −OAc, $-CH_2OH$, $-CH_2OAc$

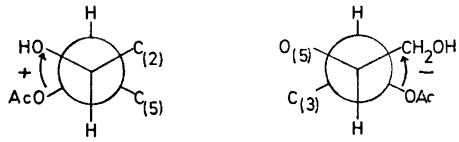
The main contribution to the Cotton effect thus arises from the presence of a neighbouring oxygen or oxymethylene function. In order to explain the results in Table 1 it is furthermore necessary to propose that the magnitude of the effect of these groupings on the observed dichroism decreases in the order

$$CH_2OH \geq CH_2OAc \gg O\text{-}5 > OH > OCH_3 > OAc$$

The expected signs for the observed dichroism following from these empirical rules are given in the last column in Table 1.

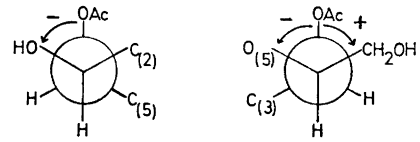
The following two examples illustrate the reasoning used in the various correlations: For methyl 4-*O*-acetyl-α-D-glucopyranoside (as well as for the

β-anomer and for methyl 4-*O*-acetyl-α-D-mannopyranoside) the units (5) and (6) would be expected to determine the sign of the CD observed.



(5) (6)

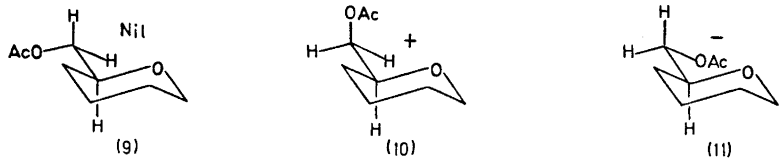
Since the contribution from (6) is thought to dominate over that from (5) the sign of the CD is predicted to be negative, in agreement with the findings shown in Table 1. On the other hand, methyl 4-*O*-acetyl-β-D-galactopyranoside would, by the same reasoning, be expected to have positive CD, arising from contributions from the units (7) and (8) and this is in agreement with the CD observed.



(7) (8)

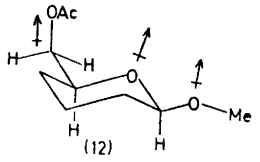
In order to explain the observed CD for the 4-acetates it is therefore necessary to postulate the dominance of the influence from the primary oxymethylene group (acetoxy or hydroxy). By contrast, this dominating influence is not observed for ring oxymethylene functions. Thus, for example, the CD for an acetyl group in the 2-position of a mannopyranoside is assumed to be relatively unaffected by the CHOAc group attached to C – 3. The reason for this apparent anomaly is not clear, but could be associated with the rotational freedom of a primary acetoxy- or hydroxymethylene group which, by contrast to the corresponding group in the pyranose ring, can adopt conformations which affect the sign of the CD strongly.

Some of the 6-*O*-acetyl derivatives give rise to two CD bands. Whenever this occurs, a substantial separation of the wave-lenghts for the CD bands is observed. This separation effect has been described and accounted for previously.[3,ab] The occurrence of the double CD bands probably is best interpreted as being due to the presence, in solution, of two conformers. For the 6-*O*-acetyl derivatives, the above rationale requires that, in accordance with previous results, conformation (9) does not give rise to CD, while those of (10) and (11) give a positive and a negative CD band, respectively.



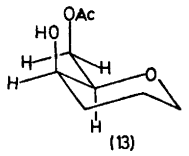
(9) (10) (11)

Hall and Manville, on the basis of NMR data, have concluded that (9) is the favoured conformation for acetylated D-*galacto*-hexopyranoses and that of (10) for the corresponding D-*gluco* isomers.[4] Lemieux and co-workers have, however, presented data from investigations of NMR and of optical rotation to support the view, that at least for D-*erythro*-hexopyranoses, conformation (11) is the favoured one.[5,6] The double CD band for methyl 6-*O*-acetyl-α-D-glucopyranoside is best explained by assuming the presence, in ethanol, of both conformations (10) and (11). For the corresponding β-anomer, however, the unfavourable dipolar interactions of conformation (10), shown in (12), should lead to the predominance, in ethanol solution, of conformation (11) and thereby a single, negative CD band, which is that observed.



(12)

By analogy, methyl 6-*O*-acetyl-α-D-mannopyranoside gives two CD bands, presumably corresponding to conformations (10) and (11). For the anomeric methyl 6-*O*-acetyl-D-galactopyranosides, conformation (10) would necessitate an unfavourable 1,3-interaction, depicted in (13).

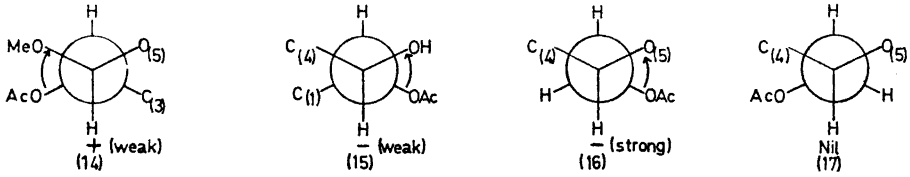


(13)

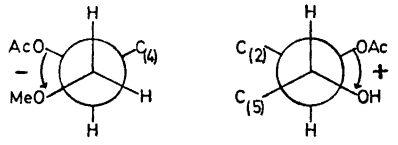
It is therefore possible that for these substances, conformation (11) predominates over (10) giving a negative, single CD band, which would fit the above generalization. In the crystalline state, methyl 6-*O*-acetyl-β-D-galactopyranoside, however, adopts conformation (9).[7] It should be noted that the presence, in the various conformational equilibria of the 6-acetates, of conformation (9) would remain undetected in the CD experiments, since (9) is expected to give a negligible contribution to the CD.*

The signs of the CD bands of the various diacetates listed in Table 1 are those expected from the above discussion, with two exceptions. The origin of the two negative CD bands for methyl 4,6-di-*O*-acetyl-β-D-mannopyranoside is not entirely clear. The sign of one CD band given by methyl 2,6-di-*O*-acetyl-β-D-galactopyranoside is opposite to that expected, since the above considerations would predict negative CD for this substance, as depicted in (14) – (17).

* The presence of several rotamers for the C(5)-CH_2OTMS groups in several monosaccharide pertrimethyl silyl derivatives has recently been demonstrated by 220 MHz ^1H NMR.[7b]



This indicates that other factors such as 1,3-diaxial type interactions may be of importance in determining the sign of the CD. In addition, methyl 3-*O*-acetyl-2-*O*-methyl-α-D-glucopyranoside does not show any detectable CD band, whereas the above rationale would predict it to be positive, (18) and (19):



This emphasizes that these rules, being entirely empirical, should be used with caution.

EXPERIMENTAL

General methods. Concentrations were performed at reduced pressure. Melting points are corrected. Optical rotations were determined at room temperature (20 – 22°) with a Perkin-Elmer 141 polarimeter. NMR spectra were recorded with a Varian A-60 A spectrometer using tetramethylsilane as internal reference and deuteriochloroform or deuteriomethanol as solvents (the latter for glycoside mono- and diacetates). The NMR spectra were invariably in accordance with the presumed structures. TLC was performed on silica gel GF^{254} (Merck). Sulphuric acid was used as spray reagent. Mallinckrodt AR silicic acid (100 mesh) was used in preparative column separations. The CD spectra were determined on a Cary 60 apparatus equipped for CD. The solvent used was ethanol throughout.

Compounds. Pertinent data for the various new compounds synthesized in the course of the investigation are summarized in Table 2. References for the various known compounds, synthesized by previously described routes, are given in Table 1.

The purity of the various acetates was checked by examining the acetates by TLC immediately after running the CD spectra (TLC solvent: ethyl acetate). All substances were found to be sufficiently stable for the purposes of the investigation.

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REFERENCES

1. Borén, H. B., Garegg, P. J., Kenne, L., Maron, L. and Svensson, S. *Acta Chem. Scand.* **26** (1972) 644.
2. Garegg, P. J. and Swahn, C.-G. *Acta Chem. Scand.* **26** (1972) 3895.

3. a. Wellman, K. M., Laur, P. A., Briggs, W. S., Moscowitz, A. and Djerassi, C. *J. Am. Chem. Soc.* **87** (1965) 66; b. Wellman, K. M., Briggs, W. S. and Djerassi, C. *J. Am. Chem. Soc.* **87** (1965) 87.
4. Hall, L. D. and Manville, J. F. *Can. J. Chem.* **47** (1969) 1.
5. Lemieux, R. U. and Stevens, J. D. *Can. J. Chem.* **43** (1965) 2059.
6. Lemieux, R. U. and Martin, J. C. *Carbohyd. Res.* **13** (1970) 139.
7. a. Lindberg, B., Garegg, P. J. and Swahn, C.-G. *Acta Chem. Scand.* **27** (1973) 380; b. Streefkerk, D. G., de Bie, M. J. A. and Vliegenhart, J. F. G. *Tetrahedron* **29** (1973) 833.
8. Hurst, D. T. and McInnes, A. G. *Can. J. Chem.* **43** (1965) 2004.
9. Bouveng, H. O. *Acta Chem. Scand.* **15** (1961) 87.
10. Whistler, R. L. and Kazeniac, S. J. *J. Am. Chem. Soc.* **76** (1954) 3044.
11. Oldham, J. W. H. and Rutherford, J. K. *J. Am. Chem. Soc.* **54** (1932) 366.
12. Müller, S., Moricz, M. and Verner, G. *Ber.* **72** (1939) 745.
13. Garegg, P. J. *Arkiv Kemi* **23** (1964) 255.
14. Kenner, J. and Richards, G. N. *J. Chem. Soc.* **1955** 1810.
15. McGilvray, D. I. *J. Chem. Soc.* **1952** 3648.
16. Bacon, J. S. D., Bell, D. J. and Lorber, J. *J. Chem. Soc.* **1940** 1147.
17. Buchanan, J. G. and Schwarz, J. C. P. *J. Chem. Soc.* **1962** 4770.
18. Freudenberg, K. and Plankenhorn, E. *Ber.* **73B** (1940) 621.
19. Dennison, J. C. and McGilvray, D. I. *J. Chem. Soc.* **1951** 1616.
20. Kiss, J. and Burkhardt, F. *Helv. Chim. Acta* **53** (1970) 1000.
21. Bourne, E. J., Stacey, M., Tatlow, C. E. M. and Tatlow, J. C. *J. Chem. Soc.* **1951** 826.

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