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CLEAVAGES OF ETHERS BY CHLOROTRIMETHYLSILANE AND ACETIC ANHYDRIDE

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Abstract - Methyl and benzyl ethers have been cleaved with a combination of reagents consisting of chlorotrimethylsilane and acetic anhydride containing a catalytic amount of concentrated sulfuric acid. Methylthiomethyl ethers yield the corresponding acetoxymethyl ethers with chlorotrimethylsilane and acetic anhydride. Comparative study with the borontrifluoride etherate and acetic anhydride method of ether cleavage suggests that chlorotrimethylsilane and acetic anhydride (con. H_2SO_4 catalysis) could be a useful alternative to it.

Protection of hydroxyl groups by making a suitable ether derivative[1] is often a practical solution in synthetic strategies but as its deprotection requires stringent reaction conditions, new methods employing mild reaction conditions compatible with various sensitive functionalities are always welcome.

It was earlier reported by us[2] that methyl and methylthiomethyl (MTM) ethers can be efficiently cleaved by chlorotrimethylsilane (CTMS) and acetic anhydride. However it was pointed out to us that this combination of reagents is not producing the desired results and on repeating the reactions given in Ref 2 again in our laboratory we confirmed that this is indeed true[3]. This led us to think that there must have been some impurity present in the CTMS sample we used for reporting our preliminary results. It was first conceived that hydrochloric acid may be present as an impurity, however, reactions carried out in the presence of a catalytic amount of HCl (gas) did not produce the desired results. Since concentrated sulfuric acid is used in the preparation of CTMS (equation 1)[4] we repeated our experiments for the cleavages of methyl ethers with CTMS/Ac_2O in the presence of a catalytic amount of concentrated sulfuric acid (method A) and the results are described in table I.

$$(Me_3Si)_2O + 2NH_4Cl + H_2SO_4 \longrightarrow 2Me_3SiCl + (NH_4)_2SO_4 + H_2O \quad ----- \quad (1)$$

Comparison of method A with BF_3/Ac_2O method (method D) reported for the cleavage of ethers by Narayanan *et al*[5] (see Table I) suggests that our method (CTMS/Ac_2O catalysed by conc. H_2SO_4) could be a useful alternative to BF_3/Ac_2O method.

Table 1[a,d]

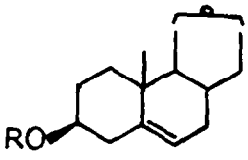
Entry	Substrate	Method	Time	Temp.	Products (% yield)
1	1b	A	10 h	24°	1c (89)
		B	20 h	24°	no reaction
		C	10 h	24°	decomposition
		D	15 h	0°	1c (93)
2	2b	A	12 h	24°	2c (51), 3(17), 4(20)
		B	24 h	24°	no reaction
		C	12 h	24°	2c (38), 3(14)
		D	15 h	0°	2c (33), 3(25), 4(25)
3	5	A	½ h	0°	6 (60)
		B	½ h	0°	6 (60)
		C	½ h	0°	6 (40)
		D	15 h	0°	6 (major)
4	7b	A	½ h	24°	7c (71)
		B	5 h	24°	no reaction
		C	½ h	24°	decomposition
		D	½ h	0°	7c (68)
5	1d	A	48 h	24°	1c (76)
		B	80 h	24°	no reaction
		C	16 h	24°	1c (53)
		D	25 h	0°	1c (77)
6	2d	A	20 h	24°	2c (82)
		B	40 h	24°	no reaction
		C	12 h	24°	2c (62)
		D	8 h	0°	2c (80)
7	1f	A	½ h	24°	1c (20), 1e (45)[b], 1a (30)
		B	½ h	24°	1c (10), 1e (55), 1a (30)
		C	½ h	24°	1c (41), 1e (15), 1a (15)
8	2f	A	1 h	24°	2c (20), 2e (40)[c], 2a (25)
		B	2 h	24°	2c (11), 2e (50), 2a (30)
		C	1 h	24°	2c (50), 2e (20), 2a (10)
9	8b	B	1 h	24°	8c (64)[d]
10	9b	B	1 h	24°	9c (84)
11	10b	B	1 h	24°	10c (84)

a) Yields reported in method D have been taken from ref. 5 in the case of substrates (1b), (2b) and (5), whereas the reaction of substrates (7b), (1d) and (2d) with BF_3/Ac_2O are being reported for the first time by us. Most of the compounds were characterised by comparison (m.p. & mixed m.p.) with their authentic samples[5] & for others data are given in the experimental section.

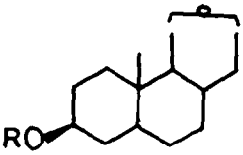
b) NMR of (1e): 5.33 s (2H,-O-CH_2O-), 5.30 m (1H, H-6), 3.70 m (1H, H-3), 2.30 s (3H, OAc).

c) NMR of (2e): 5.36 br s (2H,-O-CH_2-O-), 3.70 m (1H, H-3), 2.33 s (3H, OAc).

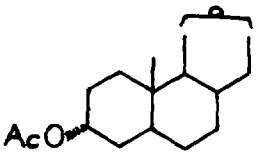
d) Substrates (1-6) and (8) belong to cholesterol series.



1a: R = H
b: R = Me
c: R = Ac
d: R = CH_2Ph
e: R = CH_2OAc
f: R = MTM



2a: R = H
b: R = Me
c: R = Ac
d: R = CH_2Ph
e: R = CH_2OAc
f: R = MTM



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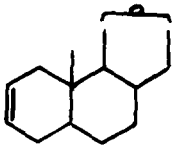

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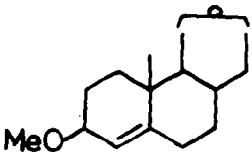

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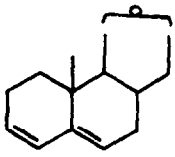

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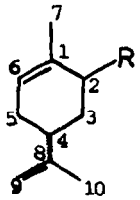
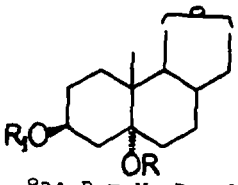
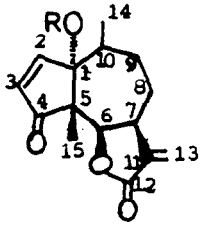


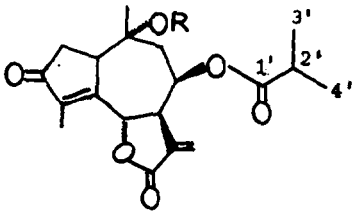
7a: R = αOH
b: R = αOMe
c: R = βOAc



8a: R = H, R_1 = Ac
b: R = MTM, R_1 = Ac
c: R = CH_2OAc, R_1 = Ac



9a: R = H
b: R = MTM
c: R = CH_2OAc



10a: R = H
b: R = MTM
c: R = CH_2OAc

Cleavage of the methyl ether of cholesterol with acetic anhydride and a catalytic amount of concentrated sulfuric acid (method C) led to complete decomposition and CTMS/Ac_2O (method B) did not cleave the methyl ethers as pointed out above. Reactions of (1b) and (2b) with CTMS and a catalytic amount of concentrated sulfuric acid furnished the starting materials and some decomposition was observed. Therefore, the role of a catalytic amount of concentrated sulfuric acid in this combination of reagents (method A) appears to be vital. It has been reported that concentrated sulfuric acid in combination with CTMS generates bis (trimethylsilyl) sulfate[6] (equation 2). Therefore, cleavage of methyl ethers (1b & 2b) with CTMS-Ac_2O containing a catalytic amount of bis (trimethylsilyl) sulfate was studied. However poor yields (20-40%) of the corresponding acetates were obtained.

$$2(CH_3)_3SiCl + H_2SO_4 \longrightarrow [(CH_3)_3Si]_2 SO_4 + 2HCl \quad \text{------ (2)}$$

As similar reaction products are obtained with method A and method D (Table I) the mechanism of the two reactions might be similar; silicon instead of boron co-ordinating with the nucleophilic oxygen of the ethers[5] leading to the cleavage of carbon oxygen bond. In the case of allylic methyl ethers compound (5) furnished the major product as cholestadiene (6) with method A and D. However carveol methyl ether (7b) was cleaved by method A and D to furnish the corresponding acetate (7c) with inversion of configuration[7].

Cleavage of benzyl ether (1d) using method A and D furnished the corresponding acetate (1c) with retention of configuration in 76% yield, the only difference being that the reaction time was longer by method A (see Table I). Cleavage of benzyl ether (2d) using method A and D furnished the acetate (2c) instead of the mixture of three products as obtained in the case of methyl ether (2b).

Cleavage of MTM ethers (8b), (9b) and (10b) with CTMS/Ac_2O (method B) furnished the corresponding acetoxymethyl ethers (8c), (9c) and (10c) respectively as the major products[8] whereas (1f) and (2f) gave mixtures of products (see table I). Acetoxymethyl ethers (8c, 9c & 10c) were also prepared from their corresponding MTM ethers by reaction with mercuric acetate in acetonitrile (see experimental). Reaction of MTM ethers (1f & 2f) with CTMS/Ac_2O catalyzed by concentrated sulfuric acid (method A) furnished a mixture of the corresponding acetoxymethyl ethers and acetates. Acetoxymethyl ethers were found to be extremely labile to mild acid and base (0.01N HCl or 1% K_2CO_3 solution in ethanol) hydrolysis to furnish the corresponding alcohols quantitatively. Since MTM ethers serve as an excellent protecting groups for alcohols - especially the tert-alcohols, the mild reaction conditions described above for their deprotection could be very useful in the case of polyfunctional molecules containing sensitive groups[8,9].

EXPERIMENTAL

General : Melting points were determined on a Kofler block and are uncorrected. IR spectra were recorded on a Perkin-Elmer 237B grating IR spectrophotometer as solutions in chloroform. NMR spectra were recorded in $CDCl_3$ on Varian T-60 instrument. Values are given in δ ppm. Low resolution MS were recorded on MS-30 instrument. Silica gel for chromatography was from E. Merck India.

General procedure for making methyl ethers :

To a stirring solution of 0.5 m mol of the substrate in 5 ml N,N-dimethylacetamide at room temperature was added 2 m mol of sodium hydride (50% dispersion in oil) after washing with dry hexane. After 2 h of stirring, 1 m mol of methyl iodide was added to the reaction mixture and the stirring continued until t.l.c.

indicated the disappearance of the starting material (6 to 8 h). Excess water was added to the reaction mixture, extracted with hexane (3 x 100 ml) and washed well with water. The extract was dried over anhydrous sodium sulphate and distilled at reduced pressure to obtain a crude residue which was purified by preparative t.l.c.

General procedure for making methylthiomethyl ethers :

To a solution of 0.5 m mol of the substrate in 2 ml acetic anhydride was added 4 ml of dimethylsulfoxide followed by 2 drops of glacial acetic acid. The reaction mixture was kept overnight at room temperature. Excess water was added, extracted with hexane (3 x 100 ml) and washed with water and dried over anhydrous sodium sulphate. Removal of solvent at reduced pressure yielded the desired product which was purified by preparative t.l.c.

General procedure for making benzyl ethers :

To a suspension of 200 mg of sodium hydride (50% dispersion in oil, washed with dry hexane) in 4 ml dry DMF was added slowly 100 mg of the substrate in 1 ml DMF at room temperature under N_2. The reaction mixture was stirred for 3 h and 0.1 ml of benzyl chloride was added over a period of 5 mint. The resulting mixture was stirred at r.t. for 12-15 h monitoring the course on t.l.c. It was diluted with cold water and extracted with dichloromethane (3 x 100 ml). The extract was washed with 5% NaOH (3 x 50 ml) and water. Evaporation of the dried extract under reduced pressure yielded the desired crude benzyl ether which was purified by preparative t.l.c.

General procedure for cleaving ethers :

Method A - With CTMS and Ac_2O catalyzed by conc. H_2SO_4:

To a solution of 0.5 m mol of the substrate in 0.5 ml dry diethyl ether was added 2 ml of acetic anhydride and 1 ml of chlorotrimethylsilane followed by one drop of concentrated sulfuric acid. The reaction mixture was left at r.t. or 0° for a period of time mentioned in table I. It was diluted with 200 ml of water and extracted with hexane (3 x 100 ml), washed with water and dried over anhydrous sodium sulphate. Distillation of the solvent at reduced pressure furnished a crude product which was purified by preparative t.l.c.

Method B - With CTMS and Ac_2O :

To a solution of 0.5 m mol of the substrate in 0.5 ml dry diethyl ether was added 2 ml of acetic anhydride and 1 ml of CTMS and the reaction mixture was left at room temperature or at 0° for a period of time mentioned in table I. It was diluted with 200 ml of water, extracted with hexane (3 x 100 ml), washed with water and dried. The solvent was removed at reduced pressure to get a residue which was purified by preparative t.l.c.

Method C - With Ac_2O and conc. H_2SO_4:

To a solution of 0.5 m mol of the substrate in 0.5 ml dry diethyl ether was added 2 ml of Ac_2O followed by one drop of conc. H_2SO_4. The reaction mixture was left at room temperature or at 0° for a period of time mentioned in table I. It was diluted with 200 ml water and extracted with hexane (3 x 100 ml). Distillation of the washed and dried extract yielded a crude product which was purified by preparative t.l.c.

Method D - With BF_3 and Ac_2O :

As mentioned in reference 5.

Reaction of (1b) with CTMS and conc. H_2SO_4 :

A solution of 100 mg of methyl ether (1b) in 2 ml dry diethyl ether was treated with 1 ml CTMS followed by one drop of concentrated sulfuric acid. The reaction mixture was left overnight at r.t. It was diluted with 200 ml water, extracted with hexane (3 x 100 ml), washed with water and dried over anhydrous sodium sulfate. Evaporation of the solvent at reduced pressure yielded 80 mg of (1b) as unreacted starting material.

Reaction of (2b) with CTMS and conc. H_2SO_4 :

Reaction of 100 mg of methyl ether (2b) with CTMS and conc. H_2SO_4 as described above furnished back 85 mg of (2b) as the unreacted starting material.

Preparation of (7b) :

Reaction of 50 mg of carveol (7a) with methyl iodide in the presence of sodium hydride in dimethylacetamide as described in the general procedure furnished on purification by preparative t.l.c. (EtOAc:Hexane, 1:15) 36 mg of carveol methyl ether (7b); NMR 5.52 m (1H, H-6), 4.79 s (2H, H-9), 3.93 m (1H, H-2), 3.49 s (3H, OMe), 2.00 s (6H, H-7 & H-10).

Cleavage of methyl ether (7b) :

Reaction of 50 mg of carveol methyl ether (7b) with CTMS-Ac_2O catalyzed by conc. H_2SO_4 as described in method A furnished on purification by preparative t.l.c. (EtOAc:Hexane, 1:10) 42 mg of (7c); NMR 5.72 m (1H, H-2), 5.30 m (1H, H-6), 4.88 s (2H, H-9), 2.20 s (3H, OAc), 2.00 br s (6H, H-7 & H-10).

Reaction of (7b) with BF_3-Ac_2O :

Reaction of 50 mg of (7b) with BF_3-Ac_2O as described in method D furnished on purification by preparative t.l.c. (EtOAc:Hexane, 1:10) 40 mg of (7c).

Preparation of (1d) :

Reaction of 100 mg of cholesterol (1a) with benzyl chloride in the presence of NaH in DMF as described in the general procedure yielded on purification by preparative t.l.c. (EtOAc:Hexane, 1:20) 62 mg of benzyl ether (1d) m.p. 117° (acetone) reported[10] m.p. 118.5°. NMR 7.30 s (5H, -Ph), 5.32 m (1H, H-6), 4.70 s (2H, O-CH_2-), 3.65 m (1H, H-3).

Preparation of (2d) :

Reaction of 100 mg of cholestan-3 β-ol (2a) with benzylchloride in the presence of NaH in DMF as described in the general procedure yielded on purification by preparative t.l.c. (EtOAc:Hexane, 1:20) 54 mg of (2d) m.p. 80°. IR bands at 2990, 1450, 1350 and 1060 cm^{-1}; NMR 7.26 s (5H, -Ph), 4.76 s (2H, O-CH_2-), 3.67 m (1H, H-3); MS m/z 478 (M^+), 387, 371 & 71.

Preparation of (1f) :

Reaction of 100 mg of (1a) with DMSO-Ac_2O as described in the general procedure furnished on purification by preparative t.l.c. (EtOAc:Hexane, 1:15) 88 mg of (1f) m.p. 115° (EtOAc). IR bands at 2900, 1455, 1370 and 1150 cm^{-1}; NMR 5.25 m (1H, H-6), 4.40 s (2H, O-CH_2-), 3.80 m (1H, H-3), 2.00 s (3H,-S-CH_3); MS m/z 446 (M^+), 369 and 71. Anal. calcd. for $C_{29}H_{50}OS$: C, 77.97; H, 11.28. Found: C, 78.28; H, 11.02.

Preparation of (2f) :

Reaction of 100 mg of (2a) with DMSO-Ac_2O as described in the general

procedure furnished on purification by preparative t.l.c. (EtOAc:Hexane, 1:20) 78 mg of (2f) m.p. 86°. NMR 4.42 s (2H, O-CH_2-), 3.78 m (1H, H-3), 2.00 s (3H, -S-CH_3); MS m/z 448 (M^+) 371 and 71.

Preparation of (8b) :

Reaction of 100 mg of (8a) with DMSO-Ac_2O as described in the general procedure furnished on purification by preparative t.l.c. (EtOAc:Hexane, 1:15) 85 mg of (8b) m.p. 135-136° (EtOAc-MeOH). IR bands at 2900, 1730, 1460, 1375 and 1250 cm^{-1}; NMR 4.35 m (1H, H-3), 4.45 s (2H, O-CH_2-S), 2.00 s (3H, S-CH_3) and 1.90 s (3H, OAc); MS m/z 506 (M^+), 463, 448, 445, 429 & 71.

Preparation of (9b) :

Reaction of 100 mg of parthenin (9a) with DMSO-Ac_2O as described in the general procedure furnished on purification by preparative t.l.c. (EtOAc:Hexane, 1:3) 80 mg of (9b) as a gum. It exhibited IR bands at 2900, 1760, 1725, 1600, 1100 and 1000 cm^{-1}; NMR 7.75 d (1H, H-2, J=6 Hz), 6.20 d (1H, H-3, J=6 Hz), 6.05 d (1H, H-13b, J=2 Hz), 5.45 d (1H, H-13a, J=2 Hz), 4.75 d (1H, H-6, J=8 Hz), 4.45 s (2H, O-CH_2-S), 3.30 m (1H, H-7), 2.00 s (3H, S-CH_3), 1.20 s (3H, H-15), 1.05 d (3H, H-14, J=7 Hz); MS m/z 322 (M^+), 275, 261, 260, 245 & 77. Anal. calcd. for $C_{17}H_{22}O_4S$: C, 63.34; H, 6.88. Found: C, 63.47; H, 6.71.

Preparation of (10b) :

A solution of 100 mg of (10a) in 1 ml DMSO was treated with 2 ml of Ac_2O as described in the general procedure. After usual work up and purification by preparative t.l.c. (EtOAc:Hexane, 1:10) yielded 92 mg of (10b) m.p. 153-154° (EtOAc). IR 2900, 1775, 1730, 1700, 1645, 1140, 1080 and 960 cm^{-1}; NMR 6.10 d (1H, H-13b, J=3.5 Hz), 5.70 m (1H, H-8), 5.50 d (1H, H-13a, J=3.5 Hz), 5.20 d (1H, H-6, J=10 Hz), 4.40 s (2H, O-CH_2-S), 3.20 m (1H, H-7), 2.00 s (3H, S-CH_3), 1.80 br s (3H, H-15), 1.05 s (3H, H-14), 1.10 d (6H, H-3' & H-4', J=7 Hz); MS m/z 408 (M^+), 348, 331, 278, 260, 242, 217, 200 and 71. Anal. calcd. for $C_{21}H_{28}O_6S$: C, 61.75; H, 6.91. Found: C, 61.83; H, 6.99.

Reaction of (8b) with Hg $(OAc)_2$:

A solution of 50 mg of (8b) in 3 ml of dry CH_3CN was treated with 50 mg of mercuric acetate and the reaction mixture was stirred for 3 h at room temperature monitoring on t.l.c. The reaction was quenched with water and extracted with chloroform (3 x 100 ml). The washed and dried extract was distilled at reduced pressure. The crude residue on purification by preparative t.l.c. (EtOAc:Hexane, 1:2) furnished 38 mg of (8c), which was found to be identical (t.l.c., IR, NMR and MS) with the product obtained from the reaction of (8a) with CTMS-Ac_2O. IR bands at 2900, 1735 (double intensity), 1460, 1375, 1250, & 1120 cm^{-1}; NMR 5.20 s (2H, -O-CH_2-O), 4.33 br s (1H, H-3), 1.90 s and 2.00 s (acetate); MS m/z 518 (M^+), 445, 432, 430, 402 & 71.

Reaction of (9b) with Hg $(OAc)_2$:

The reaction of 50 mg of (9b) with Hg $(OAc)_2$ as described earlier furnished after purification by preparative t.l.c. EtOAc:Hexane, 1:1) 40 mg of (9c). IR bands at 2900, 1760, 1735, 1180, 1080 and 1000 cm^{-1}; NMR 7.72 d (1H, H-2, J=6 Hz), 6.40 d (1H, H-3, J=6 Hz), 6.20 d (1H, H-13b, J=2 Hz), 5.58 d (1H, H-13a, J=2 Hz), 5.20 s (2H, O-CH_2-O), 4.80 d (1H, H-6, J=8 Hz), 3.30 m (1H, H-7), 1.98 s (3H, OAc) 1.20 s (3H, H-15), 1.05 d (3H, H-14, J=7 Hz); MS m/z 334 (M^+), 291, 276, 246 and 71. Anal. calcd. for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.71; H, 6.51.

Reaction of (10b) with $Hg(OAc)_2$:

The reaction of 50 mg of (10b) with $Hg(OAc)_2$ as described earlier furnished after purification by preparative t.l.c. (EtOAc:Hexane, 1:6) 40 mg of (10c). IR bands at 2950, 1775, 1730, 1715, 1650, 1150, 1115, 1015 and 950 cm^{-1}. NMR 6.10 d (1H, H-13b, J=3.5 Hz), 5.70 m (1H, H-8), 5.58 d (1H, H-13a, J=3.5 Hz), 5.15 s (2H, $O-CH_2-O$), 5.05 m (1H, H-6), 3.40 m (1H, H-7), 1.92 s (3H, OAc), 1.81 br s (3H, H-15), 1.05 s (3H, H-14), 1.12 d (6H, H-3' & H-4', J=7 Hz); MS m/z 420 (M^+), 377, 362. Calcd. for $C_{22}H_{28}O_8$: C, 62.85; H, 6.71. Found: C, 62.98; H, 6.82.

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6. W. Patnode and F.C. Schmidt, J. Am. Chem. Soc., 1945, 67, 2272.
7. For mechanism of the reaction explaining the formation of acetates with inversion of configuration see reference 5. Comparison of the NMR spectra of the two acetates (C-2 epimers of 7c) did not clearly reveal the difference therefore they were hydrolysed (K_2CO_3-MeOH) to their corresponding alcohols whose NMR spectra discerned the difference between the two epimers. NMR of (7a): 5.50 m (1H, H-6), 4.80 s (2H, H-9), 4.20 m (1H, H-2, $W_{\frac{1}{2}h}$= 20 Hz), 2.96 s (1H, -OH), 2.00 br s (6H, H-7 & H-10). NMR of C-2 epimer of (7a): 5.56 m (1H, H-6), 4.84 s (2H, H-9), 4.10 m (1H, H-2, $W_{\frac{1}{2}h}$= 10 Hz), 2.70 s (1H, -OH), 2.03 br s (6H, H-7 & H-10).
8. D.N. Sarma, N.C. Barua and R.P. Sharma, Chem. & Ind. (London), 1984, 223.
9. Methylthiomethyl ethers of tert-alcohols can be obtained in good yield using DMSO/Ac_2O and a small amount of glacial acetic acid e.g. see P.M. Pojer and S.J. Angyal, Aust. J. Chem., 1978, 31, 1031.
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