Electron Impact Studies. Part XCIV.[1] Retro-Diels–Alder Reaction in Negative-ion Mass Spectrometry. Nitro-2*H*,4*H*-1,3- and -2,3-dihydro-1,4-benzodioxins

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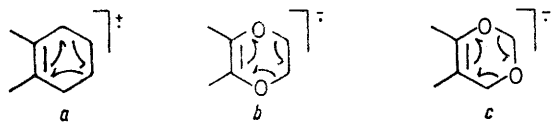
The first examples of specific retro-Diels–Alder reactions occurring from negative ions are reported for nitro-2*H*,4*H*-1,3- and -2,3-dihydro-1,4-benzodioxins. The extent of the retro-reaction from the nitro-1,3-benzodioxins is dependent upon the position of the nitro-group relative to the oxygenated ring. The fragmentation of model compounds has been used in order to rationalise the mechanism(s) of the various rearrangement processes.

ORGANIC compounds containing suitable functional groups yield pronounced molecular anions at 70 eV [2-4] by secondary electron capture processes.[5-7] Many molecular anions formed by secondary electron capture undergo unimolecular fragmentation, and we have described such fragmentations for various organic functional groups.[4] If the internal energy of a molecular anion is insufficient to allow cleavage of a particular functional group, then collision excitation [8-10] may be used to promote fragmentation in the negative mode.[11-14]



a *b* *c*

The most diagnostic reaction observed in the *positive* ion mass spectra of systems containing the cyclohexene system is the retro-Diels–Alder process *a*.[15] This nomenclature is also used to describe analogous six-membered ring cleavages irrespective of the nature of the atoms comprising the ring system or of the substituents attached to that ring.[16]

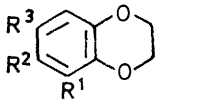
Retro-Diels–Alder reactions of cyclohexene systems are unlikely to occur in negative ion spectra because C–C bond cleavage of this type (*cf. a*) is not a favourable process in the negative mode. Fragmentation should however be effected if suitable atoms, which promote decomposition, could be placed α to the desired positions of bond cleavage. One of the most ready bond cleavages of negative ions is that which occurs α to oxygen,[17] and consequently, two systems which should undergo the retro-Diels–Alder reaction are those dioxins containing 1,4- and 1,3-oxygen atoms. The retro-processes expected would be those shown in *b* and *c* respectively. Such systems will not produce negative ions without the presence of a suitable electron capture group, and therefore the compounds chosen for study were nitro-2*H*,4*H*-1,3- and -2,3-dihydro-1,4-benzodioxins.

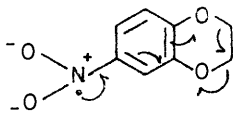
This paper describes experiments which were designed (i) to determine the extent of the retro-Diels–Alder reaction in these systems, and (ii) to study the mechanism(s) of any such reactions, with particular reference to the possible function of the nitro-group in directing the fragmentation.

RESULTS AND DISCUSSION

The spectra of the nitrobenzodioxins are listed in Table 1. All fragmentations mentioned in the text have been substantiated by the presence of metastable ions formed in both field-free regions of the mass spectrometer.[14]

(a) *Nitro-1,4-benzodioxins.*—The molecular anions of the two nitro-1,4-benzodioxins (1) and (2) undergo





d

	R^1	R^2	R^3
(1)	NO_2	H	H
(2)	H	NO_2	H
(3)	H	NO_2	NO_2

successive losses of ethylene, nitric oxide, and carbon monoxide to the same extent (Table 1), with the abundances of the $(M - C_2H_4)^-$ peaks comprising 15% of the base peak in both spectra. The ion produced by the

[1] Part XCIII, J. H. Bowie and B. D. Williams, *Austral. J. Chem.*, in the press.
[2] M. von Ardenne, K. Steinfelder, and R. Tümmler, 'Electronenanlagerungs—Massenspectrographic organischer Substanzen,' Springer Verlag, Berlin–Heidelberg–New York, 1971.
[3] J. G. Dillard, *Chem. Rev.*, 1973, **73**, 589.
[4] J. H. Bowie and B. D. Williams, 'Negative-ion Mass Spectrometry of Organic, Organometallic and Co-ordination Compounds,' in M.T.P. International Review of Science, Physical Chemistry, Mass Spectrometry, ed. A. Maccoll, Butterworths, London, vol. 2, 1975.
[5] J. C. J. Thynne, *Chem. Comm.*, 1968, 1075.
[6] T. McAllister, *Chem. Comm.*, 1972, 245.
[7] J. H. Bowie and A. C. Ho, *Austral. J. Chem.*, 1973, **26**, 2009 and references cited therein.
[8] K. R. Jennings, *Internat. J. Mass Spectrometry Ion Phys.*, 1968, **1**, 227.
[9] W. F. Haddon and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1968, **90**, 4745.
[10] F. W. McLafferty, R. Kornfeld, W. F. Haddon, K. Levsen, I. Sakai, P. F. Bente, S.-C. Tsai, and H. D. R. Schuddemage, *J. Amer. Chem. Soc.*, 1973, **95**, 3886 and references cited therein.
[11] J. H. Bowie, *J. Amer. Chem. Soc.*, 1973, **95**, 5795.
[12] J. H. Bowie, *Austral. J. Chem.*, 1973, **26**, 2719.
[13] J. H. Bowie, *Org. Mass Spectrometry*, 1974, **9**, 304.
[14] J. H. Bowie and S. G. Hart, *Internat. J. Mass Spectrometry Ion Phys.*, 1974, **13**, 319.
[15] H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, 1965, **21**, 1855.
[16] H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden Day, San Francisco–Cambridge–London–Amsterdam, 1966, pp. 209, 253, 315, 319, 586–592.
[17] J. H. Bowie and A. C. Ho, *Austral. J. Chem.*, 1971, **24**, 1093.

retro-process from the molecular anion of the dinitro-compound (3) is the base peak in this spectrum. Other fragmentations in these spectra are characteristic of aromatic nitro-compounds.[18,19] The spectra show (i) that the extent of the retro-cleavage is dependent upon the number of nitro-groups, and (ii) that the distance of the nitro-group from the oxygen atoms does *not* affect the extent of the retro-reaction *if* that nitro-group is in

TABLE 1

Negative ion mass spectra of nitro-1,3- and -1,4-benzodioxins

(A) Nitro-1,4-benzodioxins

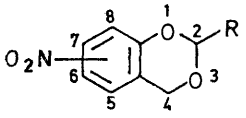
Compound	$M^{-\cdot}$	$(M - C_2H_4)^{-\cdot}$	$(M - NO\cdot)^-$	$(M - NO_2\cdot)^-$	$(M - C_2H_4 - NO\cdot)^-$	$(M - C_2H_4 - NO\cdot - CO)^-$	NO_2^-
(1)	100	15	2		1	0·3	40
(2)	100	15	3		1	0·2	10
(3)	85	100	46	8	9	3	27

(B) Nitro-1,3-benzodioxins

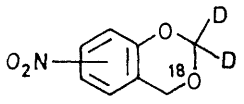
Compound	$M^{-\cdot}$	$(M - RCHO)^{-\cdot}$	$(M - RCHO - H\cdot)^-$	$(M - RCHO - HO\cdot)^-$	$(M - RCHO - NO\cdot)^-$	$(M - RCHO - NO\cdot - CO)^-$	NO_2^-
(4)	83	100	26	13	9	2	30
(5)	100	6·5			0·5	0·2	8
(6)	9	100			3·5	1·0	5
(7)	100	10			0·8	0·2	43
(8)	100	90	10	11	12	4	30
(9)	100	9			3	0·3	8
(10)	82	100			3	0·2	33
(11)	100	5			1	0·2	30

conjugation with one of the ring oxygens. No conclusion can be drawn from these spectra whether the mechanism of these retro-reactions is as shown in *b* or whether the nitro-group specifically directs the reaction (*e.g. d*).

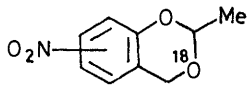
(b) *Nitro-1,3-benzodioxins.*—The spectra of 5-, 6-, 7-, and 8-nitro-1,3-benzodioxins (4)—(7) and of the corresponding 2-methylnitro-1,3-benzodioxins (8)—(11) are recorded in Table 1. The labelled compounds (12)—(17)



	NO_2	R
(4)	5	H
(5)	6	H
(6)	7	H
(7)	8	H
(8)	5	Me
(9)	6	Me
(10)	7	Me
(11)	8	Me



NO_2
(12) 5
(13) 6
(14) 7



NO_2
(15) 5
(16) 6
(17) 7

were prepared in order to determine the specificity of the retro-reactions.

The spectra of (4)—(7) and (8)—(11) show the operation of the fragmentations $M - CH_2O - NO\cdot - CO$ and M — MeCHO — NO· — CO respectively. The corresponding decompositions of the molecular anions of the $^2H_2$–^{18}O labelled derivatives (12)—(14) * and the ^{18}O compounds (15)—(17) show that the initial retro-Diels–Alder rearrangement comes specifically from the 2 and 3 positions with no atom scrambling accompanying or preceding the reaction in either the source, or field-free regions of the mass spectrometer. The spectra of (12)—(14) demonstrate that the process M — NO· does not occur. *The relative abundances of peaks produced by the retro-processes in* (4)—(11) *show that the extent of the reaction is largely dependent upon the position of the nitro-group. The order observed is* 7-NO_2 > 5-NO_2 ⩾ 6-NO_2 ≃ 8-NO_2.

This abundance ratio appears unusual, because cleavage of the phenolic O–C bond must be favoured in those systems where the nitro-group is conjugated with the phenolic oxygen, *viz.* for the 6- and 8-nitro-compounds. If the initial cleavage of this O–C bond controls the rate of reaction, the 6- and 8-nitro-compounds should undergo the *more* pronounced retro-actions. The observed ratio deviates markedly from this expectation. We therefore examined the spectra of the model compounds (18)—(25) in order to clarify the effect of the nitro-group on the relative extents of the *initial* aryl O–C or benzylic C–O bond scission.

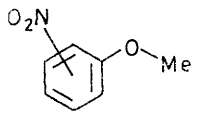
The spectra of the nitroanisoles [19] (18)—(20) and of the nitrobenzyl methyl ethers (21)—(23) show $(M -$ Me·$)^-$ and $(M -$ MeO·$)^-$ peaks respectively, with the abundances of fragment ions being in the order *para* > *ortho* ⩾ *meta* [exact abundances measured relative to the $M^{-\cdot}$ (base peak) are shown]. These results confirm that the position of the nitro-group relative to the fragmenting site markedly affects the abundance of the fragment anion. It also explains why the retro-process is more pronounced for the 7-nitro- than for the 5-nitro-1,3-benzodioxins, because in the former, the nitro-substituent is *para* to the CH_2–O groups whereas in the latter it is *ortho*. The relative extent of the initial cleavages of the

* The incorporation of label is $^2H_2$ 100%, ^{18}O 20%.

[18] C. L. Brown and W. P. Weber, *J. Amer. Chem. Soc.*, 1970, **92**, 5775.

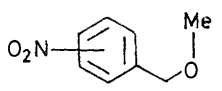
[19] J. H. Bowie, *Org. Mass Spectrometry*, 1971, **5**, 945.

aryl O–C and benzylic C–O bonds can be determined for two cases from the spectra of (24) and (25). Pronounced loss of CD_3· occurs from the molecular anion of



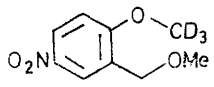
$(M - Me^{\cdot})^-$

(18) *o* 10%
(19) *m* 1%
(20) *p* 30%

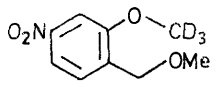


$(M - MeO^{\cdot})^-$

(21) *o* 5%
(22) *m* 0·5%
(23) *p* 12%

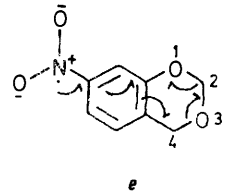


(24) M^- = 22%
$(M - CD_3^{\cdot})^-$ = 100%
$(M - MeO^{\cdot})^-$ = 0%

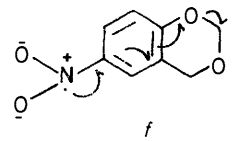


(25) M^- = 100%
$(M - MeO^{\cdot})^-$ = 3%
$(M - CD_3^{\cdot})^-$ = 6%

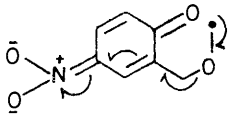
(24), whereas the abundance of the $(M - CD_3\cdot)^-$ ion is greater than that of the $(M - MeO\cdot)^-$ ion for (25), a case where loss of CD_3· is *unfavourable* [*i.e.* the NO_2 and OCD_3 groups of (25) are *meta* to each other].



e



f

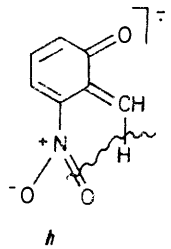


g

The evidence outlined above suggests that the observed abundances of fragment ions produced by the retro-processes from the various isomers are best rationalised in terms of the reactions being dependent upon the relative ease of cleavage of the *second bond*. We suggest that the facile cleavage of the O(1)–C(2) bond of the 5- and 7-nitro-isomers points to the operation of a retro-process of low activation energy, *i.e.* reaction *e* (for the 7-nitro-case).* The relative difficulty of O(3)–C(4) bond cleavage for the 6- and 8-nitro-isomers indicates a process of *higher* activation energy, *i.e.* the stepwise process *f* ⟶ *g* (for the 6-nitro-case).

Qualitative estimates of both the relative rates and activation energies † of two competing fragmentations from a molecular ion may be determined by observing the changes in relative abundances of the appropriate collision induced dissociations as the pressure of collision gas is increased, *i.e.* as the internal energy of the decomposing molecular species is increased.[14,22-24] We have measured the negative ion kinetic energy spectra [14] of (4)—(11) using pressures of added collision gas (N_2) ranging from 5×10^{-6} to 5×10^{-4} Torr in the first field-free region of the mass spectrometer. The abundances of ions produced by the collision-induced M — RCHO process were compared with those of the cleavage process $M \longrightarrow NO_2^-$. The i.k.e. spectra of (4), (6), (8), and (10) (the 5- and 7-nitro-isomers) showed that $k_{(M \to NO_2^-)} > k_{(M-RCHO)^-}$ with increasing collision gas pressure, whereas those of (5), (7), (9), and (11) (the 6- and 8-nitro-isomers) showed the reverse effect, *i.e.* $k_{(M-RCHO)^-} > k_{(M \to NO_2^-)}$ with increasing pressure. If it is assumed that the relative increase in the rates of NO_2^- formation (with increasing internal energy of the decomposing ion) are comparable in these cases, then the former retro-process is the one of lower activation energy, and the latter has the higher energy requirement.‡

Finally, a specific *ortho* effect involving the loss of an hydroxyl radical from the $(M - RCHO)^-$ ion is observed in the spectra (Table 1) of the 5-nitro-compounds (4) and (8). The atoms eliminated are shown in *h*. *ortho*-Effects of this type are common in negative ion spectra.[4]



h

* There is no evidence to suggest whether this process is concerted or stepwise.

† Relative activation energies can also be determined from appearance potential measurements. The molecular and $(M - RCHO)^-$ ions from (4)—(7) are formed near 0 eV (by resonance capture) and above 15 eV (by secondary electron capture). A method for the determination of relative appearance potentials for some ions produced by secondary electron capture has been described.[20] The method relies upon obtaining parallel plots in the 15—30 eV region for the standard and the peak being measured. The appropriate plots (measured with a Dynaspec ICR 9 spectrometer [21]) for ions from (4)—(7) were not parallel in this region.

‡ A referee has suggested that the differences in the retro-processes may in part be due to differing $N(E)$ *versus* E curves for the various molecular anions, *i.e.* that particular molecular anions may simply not have the energy to fragment.

EXPERIMENTAL

All spectra were measured at 70 eV, and a source pressure of 2×10^{-6} Torr, with an Hitachi–Perkin-Elmer RMU 7D mass spectrometer, modified as previously described.[14] The negative i.k.e. technique has been reported.[14]

[20] J. H. Bowie and B. Nussey, *Org. Mass Spectrometry*, 1974, **9**, 310.
[21] J. H. Bowie and B. D. Williams, *Austral. J. Chem.*, 1974, **27**, 769.
[22] D. H. Williams and R. G. Cooks, *Chem. Comm.*, 1968, 663.
[23] F. W. McLafferty and R. B. Fairweather, *J. Amer. Chem. Soc.*, 1968, **90**, 5915.
[24] I. Howe in 'Mass Spectrometry,' Specialist Periodical Reports, ed. D. H. Williams, Chemical Society, London, 1973, vol. 2, p. 36.

M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. Light petroleum had b.p. 40—60°.

Nitro-1,4-benzodioxins.—2,3-Dihydro-6-nitro- [25] and -6,7-dinitro-1,4-benzodioxin [26] were prepared by reported procedures.

2,3-*Dihydro-5-nitro-1,4-benzodioxin* (1). Treatment of 3-nitrocatechol [27] (500 mg) with ethylene dibromide (2·19 g) and potassium carbonate (500 mg) in ethylene glycol (5 cm³) by the standard method,[26] gave a crude product which was purified by chromatography in benzene over silicic acid (Mallinckrodt greater mesh; 10 g) to yield the *benzodioxin* (192 mg, 33%), which was crystallised from aqueous ethanol as yellow needles, m.p. 60—61° (Found: C, 53·3; H, 4·0; N, 7·5. $C_8H_7NO_4$ requires C, 53·05; H, 3·9; N, 7·7%).

Nitro-1,3-benzodioxins.—5-,[28] 6-,[29] and 7-Nitro-1,3-benzodioxin [30] were synthesised by known methods. The following known and unknown intermediates were used for subsequent synthesis: 2-hydroxy-5-nitrobenzyl chloride,[31] 2-hydroxy-3-nitrobenzyl alcohol,[32] 2-hydroxy-4-nitrobenzyl alcohol,[33] and 2-hydroxy-5-nitrobenzyl alcohol.[34]

2-*Hydroxy-4-nitrobenzyl bromide.* A mixture of 7-nitro-1,3-benzodioxin (300 mg) and aqueous hydrogen bromide (5 ml, 48%) was heated under reflux for 1 h, cooled, and the solid removed and crystallised from benzene–light petroleum to yield 2-*hydroxy-4-nitrobenzyl bromide* (300 mg, 78%) as pale yellow needles, m.p. 112—114° (Found: C, 36·5; H, 2·7; N, 6·1. $C_7H_6BrNO_3$ requires C, 36·2; H, 2·6; N, 6·0%).

2-*Hydroxy-6-nitrobenzyl bromide.* Treatment of 5-nitro-1,3-benzodioxin (500 mg) with aqueous hydrogen bromide (5 ml, 48%), as above, gave 2-*hydroxy-6-nitrobenzyl bromide* (520 mg, 80%) which crystallised from light petroleum–benzene as yellow needles, m.p. 140—141° (Found: C, 36·5; H, 2·6; N, 6·0. $C_7H_6BrNO_3$ requires C, 36·2; H, 2·6; N, 6·0%).

2-*Hydroxy-6-nitrobenzyl alcohol.* 2-Hydroxy-6-nitrobenzyl bromide (150 mg) was heated under reflux with water (5 cm³) for 2 h to yield 2-*hydroxy-6-nitrobenzyl alcohol* (90 mg, 82%) which crystallised from water as yellow needles, m.p. 96—98° (Found: C, 49·7; H, 4·1; N, 8·0. $C_7H_7NO_4$ requires C, 49·7; H, 4·1; N, 8·3%).

8-*Nitro-1,3-benzodioxin* (7).—To a mixture of 2-hydroxy-3-nitrobenzyl alcohol (200 mg) and aqueous formaldehyde (100 mg, 40%) was added concentrated sulphuric acid (1 cm³) and the mixture was stirred at room temperature for 1 h. The product mixture was chromatographed in benzene over silicic acid to yield 8-*nitro-1,3-benzodioxin* (40 mg, 18%), which was crystallised from ethanol as pale yellow needles, m.p. 115—116° (Found: C, 53·1; H, 3·9; N, 7·7. $C_8H_7NO_4$ requires C, 53·0; H, 3·9; N, 7·7%).

The 2-methylnitro-1,3-benzodioxins (8)—(11). 2-Methyl-6-nitro-1,3-benzodioxin has been reported.[35] The other isomers were formed by the following general procedure. A mixture of the benzyl alcohol (100 mg), acetaldehyde (5 cm³), and a catalytic amount of toluene-*p*-sulphonic acid was heated under reflux for 10 h. Removal of the acetaldehyde gave a solid which was chromatographed in benzene over silicic acid. All products were crystallised from ethanol as needles.

TABLE 2

Physical constants of compounds (8), (10), and (11)

Compound	M.p. (°C)	Yield (%)	Found (%) [a] C	H	N
(8)	82—83	82	55·3	4·6	7·2
(10)	126—127	87	55·3	4·8	7·2
(11)	74—75	63	55·2	4·9	7·0

[a] $C_9H_9NO_4$ requires C, 55·4; H, 4·6; N, 7·2%.

Labelled Compounds (12)—(17).—4-, 5-, *and* 6-*Nitro-2-hydroxybenzyl* [^{18}O]*alcohol.* Treatment of 2-hydroxy-4-nitrobenzyl bromide, 2-hydroxy-5-nitrobenzyl chloride, or 2-hydroxy-6-nitrobenzyl bromide (500 mg) by heating under reflux with $H_2{}^{18}O$ (0·1 cm³; ^{18}O = 20%), silver oxide (500 mg), and dioxan (5 cm³) for 10 h gave the appropriate [^{18}O]alcohol [4-nitro (300 mg, 82%); 5-nitro (305 mg, 67%); 6-nitro (290 mg, 80%)] which crystallised from water as yellow needles, m.p. 126—127, 125—126, and 95—96° respectively.

5-, 6-, *and* 7-*Nitro*[2,2-$^2H_2$,3-^{18}O]-1,3-*benzodioxin* (12)—(14).—Treatment of the appropriate [^{18}O] alcohol (50 mg) with aqueous [$^2H_2$]formaldehyde (25 mg; $^2H_2$ = 100%) and concentrated sulphuric acid (1 cm³) [as described for (7)], gave the doubly labelled nitro-1,3-benzodioxin which was purified by preparative thick layer chromatography on silicic acid, followed by crystallisation from aqueous ethanol to yield pale yellow needles.

TABLE 3

Physical data for compounds (12)—(14)

Compound	M.p. (°C)	Yield (%)	Incorporation (%)
(12)	76—77	60	$^2H_2$ 100; ^{18}O 20
(13)	148—150	41	$^2H_2$ 100; ^{18}O 20
(14)	92—93	68	$^2H_2$ 100; ^{18}O 20

2-*Methylnitro*[3-^{18}O]-1,3-*benzodioxins* (15)—(17). These were prepared from the three ^{18}O-labelled alcohols above by the general procedure outlined for (8)—(11).

TABLE 4

Physical data for compounds (15)—(17)

Compound	M.p. (°C)	Yield (%)	Incorporation (%)
(15)	82—83	87	^{18}O 20
(16)	113—114	65	^{18}O 20
(17)	126—127	87	^{18}O 20

Model Compounds (24) *and* (25).—2-[$^2H_3$]*Methoxy-5-nitrobenzyl methyl ether* (24). 2-Hydroxy-5-nitrobenzylmethyl ether [36] (50 mg) was heated under reflux with [$^2H_3$]methyl iodide (50 mg; $^2H_3$ = 100%), silver oxide

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(100 mg), and acetone (5 cm^3) for 10 h. Filtration, removal of the solvent, and crystallisation from light petroleum gave 2-[$^2H_3$]*methoxy-5-nitrobenzyl methyl ether* (48 mg, 88%; $^2H_3$ = 100%) as crystals, m.p. 65—67°.

2-*Hydroxy-4-nitrobenzyl methyl ether*. The reaction between 2-hydroxy-4-nitrobenzyl bromide (300 mg), silver oxide (300 mg), and methanol (5 cc) gave 2-*hydroxy-4-nitrobenzyl methyl ether* (174 mg, 74%), which was crystallised from light petroleum as yellow needles, m.p. 79—80° (Found: C, 52·5; H, 5·0; N, 7·6. $C_8H_9NO_4$ requires C, 52·5; H, 4·9; N, 7·6%).

2-[$^2H_3$]*Methoxy-4-nitrobenzyl methyl ether* (25). This was prepared from 2-hydroxy-4-nitrobenzyl methyl ether as for (24) in 92% yield, m.p. 79—80°, $^2H_3$ = 100%.

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