Regioselective Cleavage Reaction of the Aromatic Methylenedioxy Ring. V.[1] Cleavage with Sodium Alkoxides–Alcohols, Potassium *tert*-Butoxide–Alcohols, Dimsyl Anion–Methyl Alcohol, Metallic Sodium–Alcohols, and Sodium Cyanide in Dipolar Aprotic Solvents

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The reaction of aromatic methylenedioxy compounds containing electron-withdrawing groups with dimsyl anion–methyl alcohol, potassium *tert*-butoxide–alcohols, and metallic sodium–alcohols in dimethyl sulfoxide (DMSO), and with sodium alkoxides–alcohols in hexamethylphosphoramide, gave 3- and 4-hydroxybenzene derivatives in good yield by regioselective attack of the alkoxide ions on the methylenedioxy ring. The formation mechanism of alkoxide ions and the effect of DMSO in the cleavage reaction of the methylenedioxy ring are discussed on the basis of proton nuclear magnetic resonance (^{1}H-NMR) spectra. The reactions of aromatic methylenedioxy compounds (3 and 22) with sodium cyanide in dipolar aprotic solvents gave 4-cyano-3-hydroxybenzene derivatives (23 and 24) by regioselective attack of the cyanide ion on the methylenedioxy ring. The reactions of aromatic methylenedioxy compounds (28—30) containing no electron-withdrawing group with MeONa–MeOH in dipolar aprotic solvents gave non-regioselective cleavage products (31 and 34).

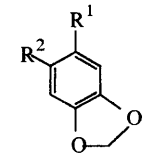
Keywords regioselective cleavage reaction; methylenedioxy ring; sodium alkoxide; dimsyl anion; potassium *tert*-butoxide; electron-withdrawing group; cyanide ion; dipolar aprotic solvent

We have previously reported[1,2] regioselective 3,4-methylenedioxy ring cleavage reactions in aromatic formyl, nitro and acetyl compounds by sodium alkoxides (RONa)–alcohols [R'OH, R=R' or R≠R', R or R'= methyl (Me), isopropyl (Me_2CH), benzyl ($PhCH_2$), phenyl (Ph), and 4-methoxyphenyl (4-$MeOC_6H_4$)] in dimethyl sulfoxide (DMSO), and have reached the following conclusions. 1) The regioselective cleavage reactions of the methylenedioxy ring with RONa–R'OH systems are achieved by the regioselective attack of the nucleophile ($R'O^-$) formed from protic solvents (R'OH) by RONa and are accelerated by adding DMSO. Namely, the alkoxide ions (MeO^-, Me_2CHO^-, $PhCH_2O^-$) formed from protic solvents attack the carbon atom at C-4 in aromatic methylenedioxy compounds to give 3-hydroxybenzene derivatives, while the phenoxide ions (PhO^-, 4-$MeOC_6H_4O^-$) attack the carbon atom of the methylenedioxy group in the compounds to give 4-hydroxybenzene derivatives. 2) The order of reactivity of the protic solvents (R'OH) used in the cleavage reactions is PhOH > 4-$MeOC_6H_4OH$ > MeOH > $PhCH_2OH$, *i.e.*, the inverse of the order of pK_a values of the protic solvents, and when the alcohols (ROH) formed from the sodium alkoxides (RONa) show smaller pK_a values than the protic solvents (R'OH) in RONa–R'OH systems, both the alcohols formed from sodium alkoxides and protic solvents act as nucleophilic reagents toward the methylenedioxy ring, as would be expected. Consequently, the alcohols formed from the sodium alkoxides in the cleavage reactions with RONa–R'OH systems must show larger pK_a values than the protic solvents if the methylenedioxy ring is to be cleaved only by the protic solvents.

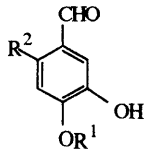
In connection with our studies on the cleavage reactions of the aromatic methylenedioxy ring, we wish to describe herein the regioselective cleavage reactions of the aromatic methylenedioxy ring in compounds containing electron-withdrawing groups with dimsyl anion–MeOH, potassium *tert*-butoxide (Me_3COK)–MeOH, and/or metallic sodium (Na)–R'OH [R'=Me, $PhCH_2$] in DMSO, as well as with RONa–R'OH (R=R' or R≠R', R or R'=Me, $PhCH_2$, Ph) in hexamethylphophoramide (HMPA), and with sodium cyanide (NaCN) in dipolar aprotic solvents, together with the cleavage reactions of the aromatic methylenedioxy ring containing no electron-withdrawing group with MeONa–MeOH in dipolar aprotic solvents.

Cleavage of Aromatic Methylenedioxy Compounds (1—3) with Dimsyl Anion–MeOH, and Me_3COK–R'OH (R'=Me, Ph) in DMSO It is well known[3] that a mixture of sodium alkoxide (RONa) and DMSO is excellently suited for the deprotonation of weakly acidic OH, NH and CH bonds. On the other hand, it is also known that the dimsyl anion ($MeSOCH_2^-$)[4] prepared from DMSO and a base such as sodium hydride (NaH) acts as a specific deprotonating agent in the Sommelet rearrangement.[5] This indicates that the cleavage reaction of the methylenedioxy ring with RONa–R'OH–DMSO systems may also be promoted by the formation of dimsyl anion from DMSO and RONa, besides the usual solvent effects of DMSO. However, Kingsbury[6] has shown that the small amounts of dimsyl anion formed from RONa–DMSO are not kinetically significant since the reaction of 2,4-dinitrochlorobenzene with potassium isopropoxide in 50% DMSO–50% isopropyl alcohol (Me_2CHOH) gives isopropyl 2,4-dinitrophenyl ether and no methylsulfinyl 2,4-dinitrophenyl ether. It is of interest to confirm the formation and action of the dimsyl anion in our cleavage reactions, and so we tried the following cleavage reactions of the methylenedioxy ring. The cleavage reactions of compounds **1**—**3** with MeOH and dimsyl anion in DMSO at room temperature gave 3-hydroxy-4-methoxybenzene derivatives (**4**—**6**) in better yields than those obtained previously by using the MeONa–MeOH–DMSO system,[2a] as shown in Table I.

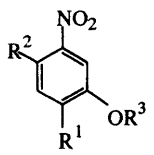
Ledwith and McFarlane[7] have reported that benzophe-



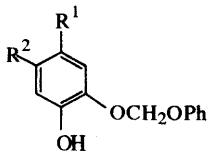
1: R^1=CHO, R^2=Br
2: R^1=CHO, R^2=H
3: R^1=NO_2, R^2=H
13: R^1=CHO, R^2=I
14: R^1=NO_2, R^2=CHO
22: R^1=NO_2, R^2=Br
28: R^1=R^2=H
29: R^1=CH=CHMe, R^2=H
30: R^1=$CH_2CH{=}CH_2$, R^2=H



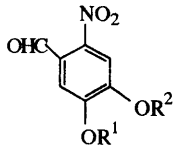
4: R^1=Me, R^2=Br
5: R^1=Me, R^2=H
7: R^1=CH_2Ph, R^2=Br
8: R^1=CH_2Ph, R^2=H
15: R^1=Me, R^2=I
19: R^1=CH_2Ph, R^2=I



6: R^1=OMe, R^2=R^3=H
9: R^1=OCH_2Ph, R^2=R^3=H
23: R^1=CN, R^2=R^3=H
24: R^1=CN, R^2=Br, R^3=H
25: R^1=CN, R^2=H, R^3=Me
26: R^1=COOMe, R^2=H, R^3=Me
27: R^1=CN, R^2=Br, R^3=Me

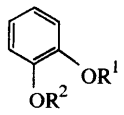


10: R^1=CHO, R^2=Br
11: R^1=CHO, R^2=Br
12: R^1=NO_2, R^2=H

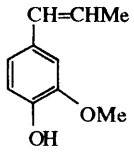


16: R^1=Me, R^2=H
17: R^1=H, R^2=Me
20: R^1=CH_2Ph, R^2=H
21: R^1=H, R^2=CH_2Ph

18



31: R^1=CH_2OMe, R^2=H
32: R^1=Me, R^2=H
33: R^1=R^2=H



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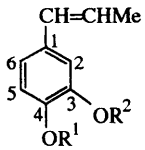

34: R^1=H, R^2=CH_2OMe
35: R^1=CH_2OMe, R^2=H
36: R^1=Me, R^2=CH_2OMe
37: R^1=CH_2OMe, R^2=Me

TABLE I. Cleavage of the Methylenedioxy Ring with MeOH and Dimsyl Anion[a] or Me_3COK[b] in DMSO

Compound (mmol)		Dimsyl anion[c] (ml)	Reaction time (h)	Product	Yield (%)	
					d)	*e*)
1[a]	1	3.0	13	**4**	75.8	67.0
2[a]	1	3.0	25.5	**5**	50.8	13.7
3[a]	1	2.0	13	**6**	76.0	73.9
1[b]	0.44		0.5	**4**	83.7	67.0
3[b]	0.50		0.5	**6**	91.6	73.9

a) Reactions at room temperature in anhydrous MeOH (1.0 ml) and DMSO (1.5 ml). *b*) Reactions with Me_3COK (1 mmol) and MeOH (0.5 ml) at 50 °C in DMSO (0.5 ml). *c*) The dimsyl anion was prepared from sodium hydride and DMSO in the usual way.[4] *d*) Isolation yield. *e*) Yield of isolated products by RONa and ROH in DMSO.[2]

none is converted to the benzophenone adduct [$(C_6H_5)_2$-C(OH)CH_2SOMe)] by the potassium salt of dimsyl anion formed from Me_3COK–DMSO. We therefore decided to use Me_3COK instead of RONa to promote the formation of the dimsyl anion and alkoxide ions ($R'O^-$) in RONa–R'OH–DMSO systems. As shown in Table I, the cleavage reactions of compounds **1** and **3** with MeOH in Me_3COK–DMSO system gave 3-hydroxy-4-methoxybenzene derivatives (**4** and **6**) in good yields. The above results indicate that the reactivity and formation of alkoxide ions ($R'O^-$) in RONa–R'OH–DMSO systems was promoted by the dimsyl anion, which may be formed through an ion-pair such as [$RO^- \cdots S^+(O^-)Me_2$] from RONa and DMSO. However, the pK_a values of DMSO, Me_2CHOH, MeOH, $PhCH_2OH$, and PhOH are *ca.* 35, *ca.* 17, *ca.* 15, *ca.* 15, and *ca.* 10, respectively. If one considers a reaction of the type shown below;

$$MeSOCH_2Na + R'OH (R' = Me, Me_2CH, PhCH_2, Ph) \rightleftharpoons MeSOMe + R'ONa$$

there will be present 1 part in 10^{20} of $MeSOCH_2Na$ in the case of MeOH and 1 part in 10^{25} of $MeSOCH_2Na$ in the case of PhOH. Consequently, $MeSOCH_2Na$ will play no significant part in the cleavage reactions even though it may be responsible for the observed exchange reactions. Hence, we tried to confirm the possibility of formation of the dimsyl anion in the RONa–ROH (R=Me, $PhCH_2$)–deuterium dimethyl sulfoxide (d_6-DMSO, $O{=}S(CD_3)_2$) system by proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy.[8a] For example, the ^{1}H-NMR spectrum of a mixture of MeONa (24.4 mg)–MeOH (0.5 ml) stirred for 70 s at room temperature, showed broad singlet signals of the methyl (δ 3.05) and hydroxyl protons (δ 5.80) of MeOH, which indicated the presence of a strong solvent–anion hydrogen bond, such as [$MeO^- \cdots$ H–OMe]. The ^{1}H-NMR spectrum of a mixture of MeOH (0.5 ml) and d_6-DMSO (0.5 ml) stirred for 70 s at 170 °C, showed a quartet signal [δ 4.04 (J=6.0 Hz)] due to the hydroxyl proton and a doublet signal [δ 3.10 (J=6.0 Hz)] due to methyl protons of MeOH, which indicated the presence of hydrogen bonds such as [MeO–H $\cdots$ $O{=}S(CD_3)_2$]. The ^{1}H-NMR spectrum of a mixture of MeOH (0.5 ml), MeONa (24.4 mg) and d_6-DMSO (0.5 ml) stirred for 70 s or for 90 min at room temperature showed the usual MeOH signals [δ 3.07 (3H, s, OMe) and δ 4.57 (1H, s, OH)][8b] together with disappearance of hydrogen bond signals [MeO–H $\cdots$ $O{=}S(CD_3)_2$] between MeOH and d_6-DMSO. The above results indicated that the methoxide ions are strongly solvated in MeOH, but are less solvated in d_6-DMSO. The ^{1}H-NMR spectrum of a mixture of MeOH (0.5 ml), MeONa (24.4 mg) and d_6-DMSO (0.5 ml) stirred for 70 s at 170 °C showed small multiplet signals due to the dimethyl moiety of DMSO at δ 2.45 (*ca.* 0.1H) together with MeOH signals [δ 3.13 (3H, s, OMe) and δ 4.89 (*ca.* 0.9H, s, OH)]. This shows that the deuterium protons of d_6-DMSO were exchanged in part with the hydroxyl proton of MeOH, yielding a small quantity of dimsyl anion from the MeONa–MeOH–d_6-DMSO system as deduced. Consequently, the effects of DMSO on the cleavage reaction are thought to be as follows. Although the cleavage reactions are promoted in part by

TABLE II. Cleavage of the Methylenedioxy Ring with RONa and R'OH in HMPA

Compound (1 mmol)	R in RONa (mmol)		R' in R'OH (ml)		HMPA (ml)	Conditions		Product	Yield (%)	
						Time (min)	Temp (°C)		*a*)	*b*)
1	Me	2.5	Me	1.0	2.5	9	150	**4**	79.6	67.0
2	Me	2.5	Me	1.0	2.5	9	150	**5**	62.6	13.7
3	Me	2.5	Me	1.0	2.5	9	150	**6**	94.6	73.9
1	$PhCH_2$	2.5	$PhCH_2$	1.0	2.5	9	150	**7**	32.1	25.0
2	$PhCH_2$	2.5	$PhCH_2$	1.0	2.5	1.4	150	**8**	25.0	23.0
3	$PhCH_2$	2.5	$PhCH_2$	1.0	2.5	1.5	150	**9**	32.0	54.0
1	Me	2.5	$PhCH_2$	1.0	2.5	9	150	**7**	42.0	
2	Me	2.5	$PhCH_2$	1.0	2.5	1.4	150	**8**	26.0	
3	Me	2.5	$PhCH_2$	1.0	2.5	1.4	150	**9**	37.0	27.0
1	Ph	2.5	Ph	1.5	2.5	20	150	**10**	47.0	55.7
2	Ph	2.5	Ph	1.5	2.5	50	150	**11**	14.6	16.6
3	Ph	2.5	Ph	1.5	2.5	25	150	**12**	56.4	43.6
2	Me	2.5	Ph	1.1	2.5	50	150	**11**	30.5	12.6
3	Me	2.5	Ph	1.1	2.5	25	170	**12**	58.7	

a) Isolation yield. *b*) Yield of isolated products by RONa–R'OH in DMSO.[2)]

the formation of a small quantity of dimsyl anion that is not kinetically significant, the big difference in activity for the alkoxide ions ($R'O^-$) formed from R'OH in the two solvent systems (RONa–R'OH and RONa–R'OH–DMSO) is attributed to the presence of strong solvent-anion hydrogen bonds in R'OH ($RO^- \cdots H\text{–}OR \rightleftharpoons RO\text{–}H \cdots {}^-OR'$) that are almost absent in DMSO, as observed in nucleophilic aromatic substitution reactions.[6,9)] This conclusion was supported by the results of the cleavage reactions of aromatic methylenedioxy compounds with RONa–R'OH–HMPA systems.

Cleavage of Aromatic Methylenedioxy Compounds (1—3) with RONa (R = Me, $PhCH_2$, Ph)–R'OH (R' = Me, $PhCH_2$, Ph) in HMPA The above consideration of DMSO effects in the cleavage reactions indicates that the cleavage reactions of the methylenedioxy ring by RONa–R'OH will be promoted on changing from protic solvents (R'OH) to dipolar aprotic solvents. Thus, we tried the cleavage reaction with RONa–R'OH in HMPA (dipolar aprotic solvent), since it is well known[10)] that HMPA promotes the ionization of hydrocarbons, and that the hydrogen of HMPA is completely unreactive to base.

As was expected, the cleavage reactions of compounds **1**—**3** with RONa–R'OH (R = R' or R ≠ R', R or R' = Me, $PhCH_2$, Ph) in HMPA gave 3-hydroxybenzene derivatives (**4**—**9**),[2)] and 4-hydroxybenzene derivatives (**10**—**12**),[1,2b)] respectively, in good yields as shown in Table II. In particular, the cleavage reactions of compounds **1**—**3** with MeONa–MeOH in HMPA were more useful than those with MeONa–MeOH in DMSO.

Cleavage of Aromatic Compounds (1—3, 13, 14) with Na–MeOH or $PhCH_2OH$ in DMSO In the cleavage reaction of the methylenedioxy ring with RONa–R'OH–DMSO (R = R' or R ≠ R', R or R' = Me, $PhCH_2$) systems, RONa used as the base must be prepared from ROH and Na under the anhydrous conditions, and must satisfy the requirement that the alcohols (ROH) formed from RONa show larger pK_a values than the protic solvents (R'OH) in the case of R = R', as described in this paper. Hence, we decided to use Na as a base instead of RONa in the cleavage reactions. The reactions of compounds **1**—**3**, **13** and **14** with Na–MeOH or Na–$PhCH_2OH$ in DMSO gave 3-hydroxybenzene derivatives (**4**—**6** and **15**—**17** or **7**—**9** and **18**—**21**), as shown in Table III. This method is convenient, and the yields of **6** and **9** obtained by the cleavage reaction of **3** were increased compared with those obtained previously[2)] by using RONa–ROH (R = Me, $PhCH_2$)–

TABLE III. Cleavage of the Methylenedioxy Ring with Sodium Metal (Na) and ROH in DMSO

Starting material (1 mmol)	Conditions[a)]	Product	Yield (%)	
			b)	*c*)
1	A	**4**	58.3	67.0
2	A	**5**	25.4	13.7
3	A	**6**	80.7	73.9
13	A	**15**	37.6	44.4
14	A	**16**	66.1	50.8
		17	3.0	25.0
1	B	**7**	17.9	25.0
1	B	**18**	14.2	
2	B	**8**	9.5	23.0
3	B	**9**	72.4	54.0
13	B	**19**	12.0	14.0
14	B	**20**	50.4	41.0
		21	6.3	

a) A, Reactions with Na (2 mmol) and anhydrous MeOH (2 ml) in DMSO (1.5 ml) at 150 °C for 3.5 min; B, Reactions with Na (2 mmol) and anhydrous $PhCH_2OH$ (1.0 ml) in DMSO (1.5 ml) at room temperature for 20 h. *b*) Isolation yield. *c*) Yields of isolated products by RONa and ROH in DMSO.[2)]

TABLE IV. Cleavage of the Methylenedioxy Ring with Sodium Cyanide

Compound (1mmol)	Solvent (ml)		Sodium cyanide (mmol)	Conditions		Product	Yield (%)[a)]
				Time	Temp. (°C)		
3	DMSO	1.5	1.0	30 min	150	**23**	19.6
	DMF	1.5	1.0	30 min	150	**23**	35.2
	HMPA	2.0	2.5	9 min	150	**23**	90.4
	MeOH	1.5	1.0	35 h	80	**4**	16.1
22	DMSO	1.5	1.0	2 min	150	**24**	5.5
	DMF	1.5	1.0	2.5 h	150	**24**	29.6
	HMPA	2.0	2.5	35 min	150	**24**	36.1

a) Isolation yield.

TABLE V. Cleavage of **28**, **29** and **30** with MeONa and MeOH in HMPA or DMSO[a]

Compound (1 mmol)	13.5% MeONa in MeOH (ml)	HMPA (ml)	DMSO (ml)	Product	Yield (%)[b]
28	1.0	1.5		**31**	61.7
28	1.0		1.5	**31**	22.0
28	2.5			No reaction	
29	1.0	1.5		(**34**+**35**)[c]	63.7
29	1.0		1.5	(**34**+**35**)[d]	20.4
29	2.5			(**34**+**35**)	2.5
30	1.0	1.5		(**34**+**35**)[e]	61.5
30	1.0		1.5	(**34**+**35**)[f]	38.8
30	2.5			(**34**+**35**)	0.7

a) The reaction was carried out for 2 h at 150 °C. *b*) Isolation yield. *c*—*f*) An inseparable mixture of **34** and **35**. *c*), *ca.* 1.0 : 1.5; *d*), *ca.* 4.0 : 1.0; *e*), *ca.* 1.0 : 1,5; *f*), *ca.* 1.6 : 1.0.

DMSO systems.

Cleavage of Aromatic Methylenedioxy Compounds (3, 22) with NaCN in Dipolar Aprotic Solvents We planned the regioselective cleavage reaction of aromatic methylenedioxy compounds with the cyanide ion (CN^-) instead of the alkoxide ion to give cyanobenzene compounds, which can easily be converted to amino, carboxyl, carbonyl and ester compounds. In dipolar aprotic solvents [DMSO, *N*,*N*-dimethyl formamide (DMF), HMPA], the reaction of compounds **3** and **22** with NaCN gave phenolic compounds [**23** ($C_7H_4N_2O_3$, mp 155—156 °C) and **24** ($C_7H_3BrNO_3$, mp 300 °C)], respectively, as shown in Table IV, and the best result was obtained in HMPA. Compounds **23** and **24** were established to be 4-cyano-3-hydroxynitrobenzene and 6-bromo-4-cyano-3-hydroxynitrobenzene, respectively, by chemical transformation, and from physical and spectral data, as described in Experimental. On the other hand, the reaction of **3** with NaCN in MeOH gave only **6** in 16.1% yield instead of **23**, by attack of the methoxide ion on the methylenedioxy ring.

Cleavage of Aromatic Methylenedioxy Compounds (28—30) with MeONa–MeOH in HMPA or DMSO We have already reported[1,2] the regioselective cleavage of 3,4-methylenedioxy aromatic compounds containing electron-withdrawing groups with RONa–R'OH in dipolar aprotic solvents. Therefore, we carried out the cleavage reaction of aromatic methylenedioxy compounds (**28**—**30**) containing no electron-withdrawing group with MeONa–MeOH in HMPA or DMSO as shown in Table V.

The reaction of compounds **28**—**30** with MeONa–MeOH in HMPA or DMSO gave phenolic products (**31** from **28** and an inseparable mixture of **34** and **35** from **29** or **30**), and the best result was obtained in HMPA. The infrared (IR) spectrum of **31** ($C_8H_{10}O_3$) showed absorption due to a hydroxy group at 3400 cm^{-1}, and the ^{1}H-NMR ($CDCl_3$) spectrum showed the presence of a methoxy group at δ 3.46 (3H, s, OCH_2OMe), a methylenedioxy group at δ 5.12 (2H, s, $OC\underline{H}_2OMe$), a hydroxy group at δ 6.07 (1H, s, OH, deformed with D_2O), and aromatic protons at δ 6.99 (4H, m). Consequently, compound **31** was established to be 2-methoxymethoxyphenol, which can easily be converted to 2-methoxyphenol (**32**) and 1,2-dihydroxybenzene (**33**). As shown in Table V, phenolic compounds ($C_{11}H_{14}O_3$) formed from **29** or **30** were assigned as an inseparable mixture of 4-hydroxy-3-methoxymethoxy-1-methylvinylbenzene (**34**) and 3-hydroxy-4-methoxymethoxy-1-methylvinylbenzene (**35**) on the basis of chemical transformation, and physical and spectral data (see Experimental). Treatment of the phenolic compounds (**34** and **35**) formed from **29** with diazomethane in diethyl ether gave an inseparable mixture (*ca.* 1.0 : 1.4) of the methyl ether derivatives (**36** and **37**), which were identified from a comparison of the ^{1}H-NMR spectrum with that of 3-methoxy-4-methoxymethoxy-1-methylvinylbenzene (**37**) prepared by methoxymethylation of isoeugenol (**38**) with methoxymethyl chloride ($MeOCH_2Cl$) (see Experimental). On the other hand, the reactions of compounds **28**—**30** with MeONa–MeOH in the absence of dipolar aprotic solvents gave essentially only the starting materials. Although the cleavage reaction of the aromatic methylenedioxy ring containing no electron-withdrawing group with MeONa–MeOH was promoted by addition of HMPA or DMSO, the reaction was nonregioselective. We are now trying to synthesize some biologically active compounds by this method.

Experimental

Melting points were determined by the capillary method and were not corrected. ^{1}H-NMR spectra were measured on a JEOL PS-100 or a JEOL JNM-FX-200 spectrometer using tetramethylsilane as an internal standard. IR spectra were recorded on a Hitachi 215 IR spectrophotometer. Mass spectra (MS) were taken with a JEOL JMS-D-300 mass spectrometer. Analytical thin layer chromatography (TLC) was performed on precoated glass plates with Merck Kieselgel $60F_{254}$ as the adsorbent. After development, the plates were air-dried, and exposed to ultraviolet (UV) light and/or sprayed with 1% cerium sulfate in 10% aqueous sulfuric acid, and heated. Preparative TLC (P-TLC) was performed on 20 × 20 cm glass plates coated with Merck Kieselgel $60PF_{254}$ as the absorbent (20 g per sheet). Column chromatography was performed on Merck Kieselgel 60 (70—230 mesh). Solvents were purified and dried by standard methods.

Cleavage of 6-Bromopiperonal (1) with MeOH and Dimsyl Anion in DMSO Dimsyl anion was prepared from DMSO (10 ml) and sodium hydride (550 mg) in the usual way.[4] A mixture of dimsyl anion (3 ml) and MeOH (2 ml) was stirred at room temperature for 10 min under nitrogen. A solution of **1** (229 mg, 1 mmol) in MeOH (1 ml) was added slowly to the reaction mixture, and the whole was further stirred at room temperature for 13 h. The reaction mixture was diluted with cold water (40 ml) and 10% NaOH (10 ml), and extracted with diethyl ether (50 ml × 2). Piperonyl alcohol (25 mg, 10.8%) was isolated from the extract. The mother liquor was acidified (pH 4—5) with concentrated HCl, and extracted with diethyl ether (50 ml × 3). The extract was washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by P-TLC (eluent benzene–acetone, 4 : 1) to give 6-bromoisovaniline (**4**, 175 mg, 75.8%), mp 107—110 °C, which was identical with authentic **4**.[2a] Compounds **2** and **3** were cleaved similarly, as shown in Table I.

Cleavage of 1 with Me_3COK and MeOH in DMSO A mixture of Me_3COK (112.2 mg, 1 mmol) and DMSO (0.5 ml) was stirred at 50 °C for 30 min, and then MeOH (0.5 ml) was added. The mixture was stirred at 50 °C for 30 min, then **1** (100 mg, 0.44 mmol) was added, and stirring was continued at 50 °C for 30 min. Work-up in the usual way gave **4** (83.7 mg, 83.0%), mp 104—107 °C.[2a] Compound **3** was cleaved similarly, as shown in Table I.

Cleavage of 1 with MeONa and MeOH in HMPA A mixture of **1** (229 mg, 1 mmol), MeONa (135 mg, 2.5 mmol), and MeOH (1.0 ml) in HMPA (2.5 ml) was stirred at 150 °C for 9 min. The reaction mixture was poured into cold water (20 ml), NaOH (30 mg) was added, and the whole was extracted with diethyl ether (50 ml × 2). Piperonyl alcohol (5 mg, 2.2%) was isolated from the extract. The mother liquor was acidified (pH 4—5) with concentrated HCl, and extracted with diethyl ether (50 ml × 3). The extract was washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by P-TLC (eluent benzene–acetone, 4 : 1) to give **4** (183.9 mg, 79.6%), mp 105—108 °C.[2a] Compounds **2** and **3** were cleaved similarly, as shown in Table II.

Cleavage of 1 with $PhCH_2ONa$ and $PhCH_2OH$ in HMPA A mixture

of **1** (229 mg, 1 mmol), $PhCH_2ONa$ (325 mg, 2.5 mmol), and $PhCH_2OH$ (1.0 ml) in HMPA (2.5 mmol) was stirred at 150 °C for 9 min. Work-up in the usual way gave **7** (98.8 mg, 32.1%), mp 123—129 °C.[2] Compounds **2** and **3** were cleaved similarly, as shown in Table II.

Cleavage of 1 with MeONa and $PhCH_2OH$ in HMPA A mixture of **1** (229 mg, 1 mmol), MeONa (135 mg, 2.5 mmol), and $PhCH_2OH$ (1.0 ml) in HMPA (2.5 ml) was stirred at 150 °C for 9 min. Work-up in the usual way gave 4-benzyloxy-6-bromo-3-hydroxybenzaldehyde (**7**, 129.2 mg, 42.0%), mp 128—129 °C, which was identical with authentic **7**.[2c] Compounds **2** and **3** were cleaved similarly, as shown in Table II.

Cleavage of 1 with PhONa and PhOH in HMPA A mixture of **1** (229 mg, 1 mmol), PhONa (290 mg, 2.5 mmol), and PhOH (1.5 ml) in HMPA (2.5 ml) was stirred at 150 °C for 20 min. Work-up in the usual way gave 6-bromo-4-hydroxy-3-phenoxymethoxybenzaldehyde (**10**, 66.8 mg, 47.0%, mp 119—120 °C, from petroleum ether–diethyl ether), which was identical with authentic **10**.[2b] Compounds **2** and **3** were cleaved similarly, as shown in Table II.

Cleavage of Piperonal (2) with MeONa and PhOH in HMPA A mixture of **2** (150 mg, 1 mmol), MeONa (135 mg, 2.5 mmol), and PhOH (1.1 ml) in HMPA (2.5 ml) was stirred at 150 °C for 50 min. Work-up in the usual way gave 4-hydroxy-3-phenoxymethoxybenzaldehyde (**11**, 43.3 mg, 30.5%), mp 115—118 °C (petroleum ether–diethyl ether), which was identical with authentic **11**.[2b] Compound **3** was cleaved similarly, as shown in Table II.

Cleavage of 1 with Na and MeOH in DMSO Na (46 mg, 2 mmol) was added to a solution of **1** (229 mg, 1 mmol) and MeOH (2 ml) in DMSO (1.5 ml), and the mixture was stirred at 150 °C for 3.5 min. MeOH was removed under reduced pressure, and the residue thus obtained was diluted with cold water (20 ml) and 10% NaOH (10 ml). Work-up in the usual way gave **4** (134.6 mg, 58.3%), mp 108—109 °C.[2a] Compounds **2**, **3**, and **13**—**14** were cleaved similarly, as shown in Table III.

Cleavage of 1 with Na and $PhCH_2OH$ in DMSO A mixture of **1** (229 mg, 1 mmol), Na (46 mg, 2 mmol) and benzyl alcohol (1 ml) in DMSO (1.5 ml) was stirred at room temperature for 20 h. Work-up in the usual way gave **7** (54.9 mg, 17.9%), mp 127—129 °C and 4-benzyloxy-6-bromo-3-hydroxybenzyl alcohol (**18**, 43.8 mg, 14.2%), mp 147—149 °C, which were identical with authentic samples **7**[2b] and **18**[2b] Compounds **2**, **3**, **13**, and **14** were cleaved similarly, as shown in Table III.

Cleavage of 3 with Sodium Cyanide in Dipolar Aprotic Solvents (i) In DMSO: A mixture of **3** (167 mg, 1 mmol) and NaCN (49 mg, 1 mmol) in DMSO (1.5 ml) was stirred at 150 °C for 30 min. The mixture was diluted with cold water (10 ml), and 5% NaOH (10 ml), then extracted with diethyl ether (50 ml × 2). The ether extract was purified by P-TLC (eluent $CHCl_3$) to give the starting material **3** (38.5 mg, 23.2%). The mother liquor was acidified (pH 4—5) with concentrated HCl and extracted with diethyl ether (50 ml × 3). The extract was washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by P-TLC (eluent $CHCl_3$–MeOH, 7:1) to give 4-cyano-3-hydroxynitrobenzene (**23**, 31.3 mg, 19.6%), mp 155—156 °C (from CCl_4). IR ν_{max} cm^{-1}: 3280 (OH), 2240, 1620 (CN), 1535, 1355 (NO_2). ^{1}H-NMR (100 MHz, $CDCl_3$) δ: 6.91 (1H, d, J=8 Hz, 5-H), 7.77 (1H, d, J=2 Hz, 2-H), 7.83 (1H, dd, J=8.0, 2.0 Hz, 6-H). *Anal.* Calcd for $C_7H_4N_2O_3$: C, 51.12; H, 2.46; N, 17.02. Found: C, 51.15; H, 2.43; N, 17.01.

(ii) In HMPA: A mixture of **3** (167 mg, 1 mmol) and NaCN (49 mg, 1 mmol) in HMPA (2 ml) was stirred at 150 °C for 1 min. Further NaCN (24.5 mg, 0.5 mmol × 3) was then added to the mixture every 1 min for 3 min under stirring at 150 °C. Work-up of the mixture as described in (i) gave **23** (148.3 mg, 90.4%), mp 156—157 °C.

(iii) In DMF: A mixture of **3** (167 mg, 1 mmol) and NaCN (49 mg, 1 mmol) in DMF (1.5 ml) was stirred at 150 °C for 30 min. Work-up of the mixture as described in (i) gave **23** (27.2 mg, 16.1%), mp 156—158 °C and unchanged starting material **3** (99.9 mg, 59.1%).

Cleavage of 3 with Sodium Cyanide in MeOH A mixture of **3** (167 mg, 1 mmol) and NaCN (49 mg, 1 mmol) in MeOH (1.5 ml) was stirred at 80 °C for 35 h. Work-up in the usual way gave **4** (27.2 mg, 16.1%), mp 107—109 °C[2] and unchanged starting material **3** (99.9 mg, 59.1%).

4-Cyano-3-methoxynitrobenzene (25) Compound **23** (24.7 mg, 0.15 mmol) was methylated with ethereal diazomethane to give **25** (16.4 mg, 61.2%), mp 175—177 °C (from ethyl acetate, lit.[11] mp 180 °C). IR ν_{max} cm^{-1}: 2230, 1615 (CN), 1535, 1355 (NO_2). ^{1}H-NMR (100 MHz, d_6-acetone) δ: 4.20 (3H, s, 3-OMe), 8.12 (3H, s, 2, 5, 6-H).

4-Carbomethoxy-3-methoxynitrobenzene (26) Dry hydrogen chloride gas was introduced into a mixture of **25** (36.3 mg, 0.2 mmol), dry MeOH (3 ml) and dry ether (3 ml) for 2 h. The mixture was allowed to stand for 12 h at room temperature, and then treated with water (20 ml), heated at 60 °C for 30 min, and extracted with $CHCl_3$. The extract was washed with water, dried ($MgSO_4$), and evaporated. The white residue was purified by P-TLC (eluent $CHCl_3$) to give **26** (15.8 mg, 37.4%), mp 86—88 °C (from MeOH, lit.[12] mp 86.5—87.1 °C). IR ν_{max} cm^{-1}: 1740, 1530, 1355 (NO_2). ^{1}H-NMR (100 MHz, $CDCl_3$) δ: 3.98 (3H, s, 3-OMe), 4.05 (3H, s, 4-COOMe), 7.85 (3H, s, 2, 5, 6-H).

Cleavage of 6-Bromo-3,4-methylenedioxynitrobenzene (22) with NaCN in DMSO A mixture of **22** (244 mg, 1 mmol) and NaCN (49 mg, 2 mmol) in DMSO (1.5 ml) was stirred at 150 °C for 2 min. After usual work-up, the reaction mixture was purified by P-TLC (eluent $CHCl_3$–MeOH, 10:3) to give a 6-bromo-4-cyano-3-hydroxynitrobenzene (**24**, 22.5 mg, 5.5%), and unchanged starting material **22** (108.6 mg, 44.5%). Compound **24** had mp 300 °C (from $CHCl_3$–MeOH). IR ν_{max} cm^{-1}: 3400 (OH), 2245, 1620 (CN), 1530, 1355 (NO_2): ^{1}H-NMR (100 MHz, CD_3OD) δ: 7.15 (1H, m, OH), 7.80 (2H, br s, 2 and 5-H). *Anal.* Calcd for $C_7H_3BrNO_3$: C, 34.60; H, 1.24; N, 11.53. Found: C, 34.80; H, 1.25; N, 11.46.

Compound **22** was also similarly cleaved with NaCN in DMF and/or HMPA, as shown in Table IV.

6-Bromo-4-cyano-3-methoxynitrobenzene (27) A solution of **24** (22.5 mg, 0.1 mmol) in MeOH (5 ml) was treated with ethereal diazomethane, and allowed to stand at room temperature for 30 min. The reaction mixture was concentrated *in vacuo*, and the residue was purified by P-TLC (eluent $CHCl_3$–benzene, 10:1) to give **27** (12.0 mg, 52.6%), mp 203—205 °C (from *n*-hexane–$CHCl_3$). IR ν_{max} cm^{-1}: 2240, 1620 (CN), 1540, 1365 (NO_2). ^{1}H-NMR (100 MHz, $CDCl_3$ δ: 3.92 (3H, s, 3-OMe), 7.37 (1H, s, 2-H), 7.87 (1H, s, 5-H). The ^{1}H-NMR spectrum of **27** showed an intramolecular nuclear Overhauser effect (NOE) increment of 22% between the methoxy protons (δ 3.92) and H-2 (δ 7.37).

Cleavage of 1,2-Methylenedioxybenzene (28) with MeONa and MeOH in Dipolar Aprotic Solvents (i) In HMPA: A mixture of **28** (122.0 mg, 1 mmol) and 13.5% MeONa–MeOH (1 ml) in HMPA (1.5 ml) was stirred at 150 °C for 2 h. The mixture was diluted with cold water (30 ml), 10% NaOH (20 ml), and extracted with diethyl ether (30 ml × 2). The ether extract was purified by P-TLC (eluent benzene) to give the starting material **28** (21.5 mg, 17.6%). The mother liquor was acidified (pH 5—6) with concentrated HCl and extracted with diethyl ether (40 ml × 3). The extract was washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by P-TLC (eluent benzene) to give 2-methoxymethoxyphenol (**31**, 95.0 mg, 61.7%, yellow oil). IR ν_{max} cm^{-1}: 3425 (OH). ^{1}H-NMR (100 MHz, $CDCl_3$) δ: 3.46 (3H, s, $OCH_2O\underline{Me}$), 5.17 (2H, s, $OC\underline{H}_2OMe$), 5.97 (1H, br s, OH, deformed with D_2O), 6.85 (4H, m, aromatic H). High-resolution MS: Calcd for $C_8H_{10}O_3$: 154.0629. Found: 154.0669.

(ii) In DMSO: A mixture of **28** (122 mg, 1 mmol) and 13.5% MeONa–MeOH (1.5 ml) in DMSO (1.5 ml) was stirred at 150 °C for 2 h. Work-up of the mixture as described in (i) gave **28** (40.3 mg, 33.0%) and **31** (44.8 mg, 30.0%).

(iii) In MeOH: A mixture of **28** (122 mg, 1 mmol) and 13.5% MeONa–MeOH (1.5 ml) was stirred at 150 °C for 2 h. Work-up of the mixture as described in (i) gave only **28** (83.5 mg, 68.4%).

Cleavage of Isosafrol (29) with MeONa and MeOH in Dipolar Aprotic Solvents (i) In HMPA: A mixture of **29** (162.0 mg, 1 mmol) and 13.5% MeONa–MeOH (1 ml) in HMPA (1.5 ml) was stirred at 150 °C for 2 h. The mixture was diluted with cold water (30 ml), and 10% NaOH (20 ml), then extracted with diethyl ether (30 ml × 2). The ether extract was purified by P-TLC (eluent $CHCl_3$) to give the starting material **29** (25.1 mg, 15.5%). The mother liquor was acidified (pH 5—6) with concentrated HCl and extracted with diethyl ether (40 ml × 3). The extract was washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by P-TLC (eluent $CHCl_3$; Rf=0.30—0.48) to give an inseparable mixture (132.5 mg, 63.7%, yellow oil, *ca.* 1.0:1.5) of phenolic compounds (**34** and **35**), which were identified from the ^{1}H-NMR spectral data. IR ν_{max} cm^{-1}: 3430 (OH). ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.82, 1.83 (totally 3H, each d, J=6.0 Hz, CH=CH$\underline{Me}$), 3.48, 3.49 (*ca.* 1.0:1.5, totally 3H, each s, $OCH_2O\underline{Me}$), 5.14, 5.17 (*ca.* 1.0:1.5, totally 2H, each s, $OC\underline{H}_2OMe$], 6.01, 6.05 (totally 1H, m, CH=C$\underline{H}$Me), 6.29 (1H, d, J=14.0 Hz, C$\underline{H}$=CHMe), 6.75, 6.87 (totally 1H, each dd, J=1.7, 8.3 Hz, 6-H), 6.87, 6.98 (totally 1H, each d, J=8.3 Hz, 5-H), 6.95, 7.08 (totally 1H, each d, J=1.7 Hz, 2-H). High-resolution MS: Calcd for $C_{11}H_{14}O_3$: 194.0941. Found: 194.0914.

(ii) In DMSO: A mixture of **29** (162 mg, 1 mmol) and 13.5% MeONa–MeOH (1.5 ml) in DMSO (1.5 ml) was stirred at 150 °C for 2 h. Work-up of the mixture as described in (i) gave **29** (17.1 mg, 10.6%) and phenolic compounds (39.6 mg, 20.4%). The phenolic compounds were identified as an inseparable mixture (*ca.* 4.0:1.0) of **34** and **35** from the ^{1}H-NMR spectral data. IR ν_{max} cm^{-1}: 3420 (OH). ^{1}H-NMR (100 MHz, $CDCl_3$) δ: 1.83 (3H, d, J=6.2 Hz, CH=CH$\underline{Me}$), 3.50 (3H, s, $OCH_2O\underline{Me}$), 5.15, 5.16 (*ca.* 4.0:1.0, totally 2H, each s, $OC\underline{H}_2OMe$), 6.08 (1H, m,

CH=CHMe), 6.30 (1H, d, J=14.5 Hz, CH=CHMe), 6.74, 6.84 (totally 1H, each dd, J=1.7, 8.0 Hz, 6-H), 6.89, 6.98 (totally 1H, each d, J=8.0 Hz, 5-H), 6.96, 7.06 (totally 1H, each d, J=1.7 Hz, 2-H). High-resolution MS: Calcd for $C_{11}H_{14}O_3$: 194.0941. Found: 194.0933.

(iii) In MeOH: A mixture of **29** (162 mg, 1 mmol) and 13.5% MeONa–MeOH (2.5 ml) was stirred at 150 °C for 2 h. Work-up of the mixture as described in (i) gave **28** (132.2 mg, 85.5%) and phenolic compounds (4.0 mg, 2.5%).

Conversion of Phenolic Compounds (34 and 35) Formed from 29 to Methyl Ether Derivatives (36 and 37) A solution of **34** (75.4 mg, 0.39 mmol) in MeOH (10 ml) was treated with ethereal diazomethane, and allowed to stand at 10 °C for 60 min. The reaction mixture was concentrated *in vacuo*, and the residue was purified by P-TLC (eluent benzene–diethyl ether, 10 : 1) to give an inseparable mixture (63.8 mg, 73.3%, yellow oil, *ca.* 1.0 : 1.4) of the methyl ether derivatives (**36** and **37**), which were identified from a comparison of the ^{1}H-NMR spectrum with that of authentic **37**. IR ν_{max} cm^{-1}: no OH. **36**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.85 (3H, dd, J=1.4, 6.3 Hz, CH=CHMe), 3.52 (3H, s, OCH_2OMe), 3.86 (3H, s, 3-OMe), 5.23 (2H, s, OCH_2OMe), 6.09 (1H, dq, J=6.3, 15.6 Hz, CH=CHMe), 6.31 (1H, dd, J=1.4, 15.6 Hz, CH=CHMe), 6.81 (1H, d, J=8.3 Hz, 5-H), 6.93 (1H, dd, J=2.2, 8.3 Hz, 6-H), 7.15 (1H, d, J=2.2 Hz, 2-H). **37**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.86 (3H, dd, J=6.4, 1.5 Hz, CH=CHMe), 3.51 (3H, s, OCH_2OMe), 3.88 (3H, s, 3-OMe), 5.21 (2H, s, OCH_2OMe), 6.11 (1H, dq, J=6.4, 15.6 Hz, CH=CHMe), 6.33 (1H, dd, J=1.5, 15.6 Hz, CH=CHMe), 6.84 (1H, dd, J=1.95, 8.5 Hz, 6-H), 6.90 (1H, d, J=1.95 Hz, 2-H), 7.07 (1H, d, J=8.5 Hz, 5-H). High-resolution MS: Calcd for $C_{12}H_{16}O_3$: 208.1097. Found: 208.1081.

Conversion of Isoeugenol (38) to 37 A mixture of **38** (1.64 g, 10 mmol), CH_2Cl_2 (20 ml), $MeOCH_2Cl$ (1.5 g, 18.6 mmol) and *N*,*N*-dimethylaniline (1.45 g, 12 mmol) was stirred at 70 °C for 7 h. The mixture was diluted with cold water (30 ml), 10% NaOH (20 ml), and extracted with diethyl ether (100 ml × 2). The extract was washed with 5% NaOH (20 ml × 2) and water (30 ml × 3), dried ($MgSO_4$), and evaporated. The residue was chromatographed on silica gel (80 g, eluent, benzene–diethyl ether, 10 : 0.5) to give **37** (1.3 g, 56.8%, yellow oil). IR ν_{max} cm^{-1}: no OH. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.86 (3H, dd, J=1.46, 6.59 Hz, CH=CHMe), 3.51 (3H, s, OCH_2OMe), 3.88 (3H, s, 3-OMe), 5.20 (2H, s, OCH_2OMe), 6.11 (1H, dq, J=6.59, 15.63 Hz, CH=CHMe), 6.34 (1H, dd, J=1.46, 15.63 Hz, CH=CHMe), 6.83 (1H, dd, J=2.0, 8.3 Hz, 6-H), 6.89 (1H, d, J=2.0 Hz, 2-H), 7.07 (1H, d, J=8.3 Hz, 5-H). High-resolution MS: Calcd for $C_{12}H_{16}O_3$: 208.1097. Found: 208.1092.

Cleavage of Safrole (30) with MeONa and MeOH in Dipolar Aprotic Solvents (i) In HMPA: A mixture of **30** (162.0 mg, 1 mmol) and 13.5% MeONa–MeOH (1 ml) in HMPA (1.5 ml) was stirred at 150 °C for 2 h. The mixture was diluted with cold water (30 ml), and 10% NaOH (20 ml), then extracted with diethyl ether (30 ml × 2). The ether extract was purified by P-TLC (eluent $CHCl_3$) to give the starting material **30** (34.1 mg, 21.0%). The mother liquor was acidified (pH 5—6) with concentrated HCl and extracted with diethyl ether (40 ml × 3). The extract was washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by P-TLC (eluent $CHCl_3$) to give an inseparable mixture (132.5 mg, 63.7%, yellow oil, *ca.* 1.0 : 1.5) of phenolic compounds (**34** and **35**), which were identified from the ^{1}H-NMR spectral data. IR ν_{max} cm^{-1}: 3430 (OH). ^{1}H-NMR (100 MHz, $CDCl_3$) δ: 1.88 (3H, d, J=6.5 Hz, CH=CHMe), 3.52 (3H, s, OCH_2OMe), 5.16, 5.18 (*ca.* 1.0 : 1.5, totally 2H, each s, OCH_2OMe), 6.08 (1H, m, CH=CHMe), 6.32 (1H, d, J=15.5 Hz, CH=CHMe), 6.77, 6.83 (totally 1H, each dd, J=1.7, 8.1 Hz, 6-H), 6.91, 6.98 (totally 1H, each d, J=8.1 Hz, 5-H), 6.95, 7.08 (totally 1H, each d, J=1.7 Hz, 2-H). High-resolution MS: Calcd for $C_{11}H_{14}O_3$: 194.0941. Found: 194.0929.

(ii) In DMSO: A mixture of **30** (162 mg, 1 mmol) and 13.5% MeONa–MeOH (1.5 ml) in DMSO (1.5 ml) was stirred at 150 °C for 2 h. Work-up of the mixture as described in (i) gave **30** (0.9 mg, 0.4%) and phenolic compounds (75.4 mg, 38.8%). The phenolic compounds were identified as an inseparable mixture (*ca.* 1.6 : 1.0) of **34** and **35** from the ^{1}H-NMR spectral data. IR ν_{max} cm^{-1}: 3425 (OH). ^{1}H-NMR (100 MHz, $CDCl_3$) δ: 1.83 (3H, d, J=6.2 Hz, CH=CHMe), 3.52 (3H, s, OCH_2OMe), 5.13, 5.15 (*ca.* 1.6 : 1.0, totally 2H, each s, OCH_2OMe), 6.05 (1H, m, CH=CHMe), 6.30 (1H, d, J=14.5 Hz, CH=CHMe), 6.75, 6.84 (totally 1H, each dd, J=1.7, 8.0 Hz, 6-H), 6.90, 6.98 (totally 1H, each d, J=8.0 Hz, 5-H), 6.96, 7.08 (totally 1H, each d, J=1.7 Hz, 2-H). High-resolution MS: Calcd for $C_{11}H_{14}O_3$: 194.0941. Found: 194.0945.

(iii) In MeOH: A mixture of **30** (162 mg, 1 mmol) and 13.5% MeONa–MeOH (2.5 ml) was stirred at 150 °C for 2 h. Work-up of the mixture as described in (i) gave **30** (126.4 mg, 77.1%) and phenolic compounds (1.3 mg, 0.7%).

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References and Notes

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