Synthesis of *E*- and *Z*-Vinyl Ethers by the Horner–Wittig Reaction

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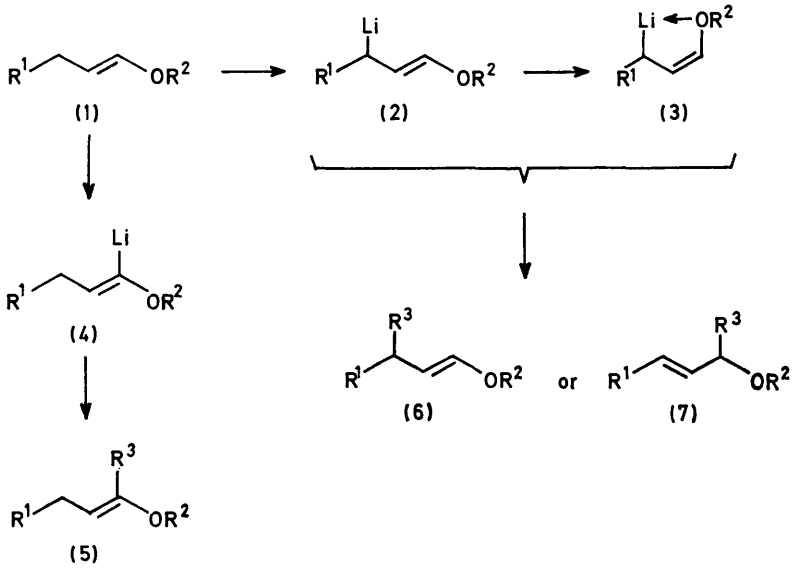
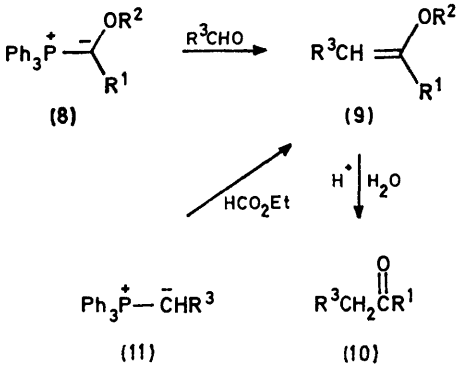
Diphenyl(methoxymethyl)- and diphenyl-(1-methoxyethyl)-phosphine oxides form lithium derivatives which add to aldehydes and ketones. The adducts may be separated into crystalline diastereoisomers each giving a single geometrical isomer of a vinyl ether on treatment with base. Hydrolysis of the vinyl ethers provides a reliable aldehyde synthesis in which the lithium derivative (19) behaves as a formyl anion equivalent. The method has been used to convert an acyl indole into a vinyl ether in compounds related to the strychnos alkaloids.

VINYL ethers [1] [*e.g.* (1)] were minor curiosities of organic chemistry, being regarded simply as derivatives of aldehydes and ketones, until the discovery of their cycloadditions to olefins,[2] their role in aliphatic Claisen reactions,[3,4] and particularly their ability to form anions.[4–6] They may form allyl [7] (2) or (3) or vinyl [8] (4) anions which react with electrophiles to give derivatives of ketones (5) or (6) or allyl alcohols (7). One important factor determining which type of anion is to be formed is the geometry of the vinyl ether: the *E*-compound (1) tends to give the vinyl 'anion' (4) and the *Z*-compound the chelated allyl 'anion' (3). Equilibration of the allyl anions (2) and (3) has been one of the few ways to make single geometrical isomers of vinyl ethers.[6,7,9]



Vinyl ethers (9) can be made by the Wittig reaction using the alkoxy-ylides (8).[1,10–14,†] This reaction has been used to convert aldehydes and ketones into the homologous aldehydes (10; $R^1 = H$) by the alkylative carbonyl transposition $R^3CHO \longrightarrow$ (10) in which the ylide (8) behaves as a formyl anion equivalent.[16] This sequence works well in some cases but is not very reliable for two main reasons: the ylides (8) are unstable [12] and the Wittig reaction often gives low yields.[17]

The cause of both these problems is probably that an oxygen atom, though electronegative, has two lone pairs of electrons and may destabilise an anion on an adjacent carbon atom.[17,18] It probably also makes the anion harder ‡ so that proton removal, particularly from enolisable aldehydes and ketones, competes with nucleophilic attack on the carbonyl group. Ylides (8) with $R^2 = Bu^n$ or *p*-MeC_6H_4 have been used [12] with some success to avoid these problems: other workers have

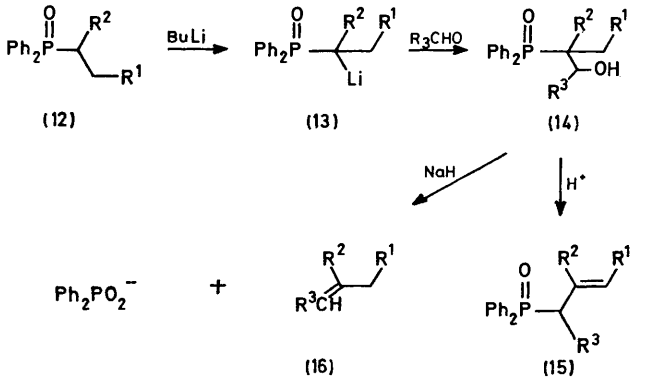


used phosphonic esters [19] and amides.[17] These methods were mostly developed as aldehyde or ketone syntheses

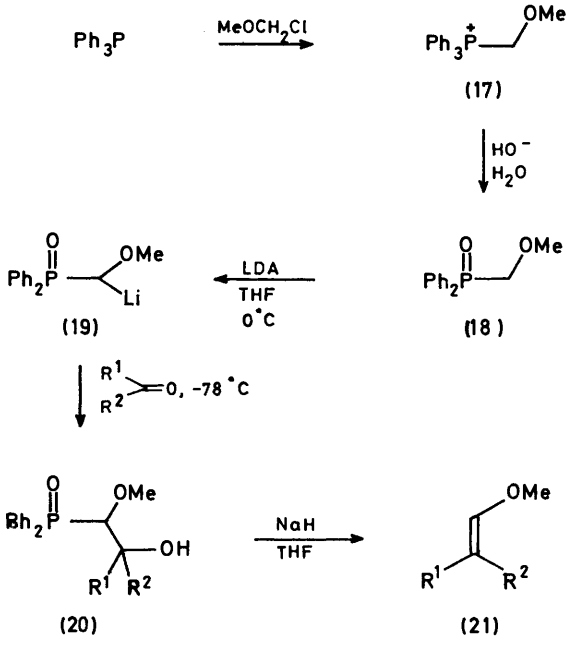
† If $R^1 = H$, normal ylides (11) and ethyl formate may be used (see ref. 15).

‡ The anion adds exclusively 1,2 to crotonaldehyde: see Entry 4, Table 1.

before the importance of vinyl ether anions was realised and so there was little interest in the stereoselectivity of the reactions. Where the ratio of geometrical isomers is reported it is usually [10,13] close to 1 : 1 though it can be as high as 9 : 1 with $(RO)_2PO{\cdot}CH(OMe)CO_2R$.[19]



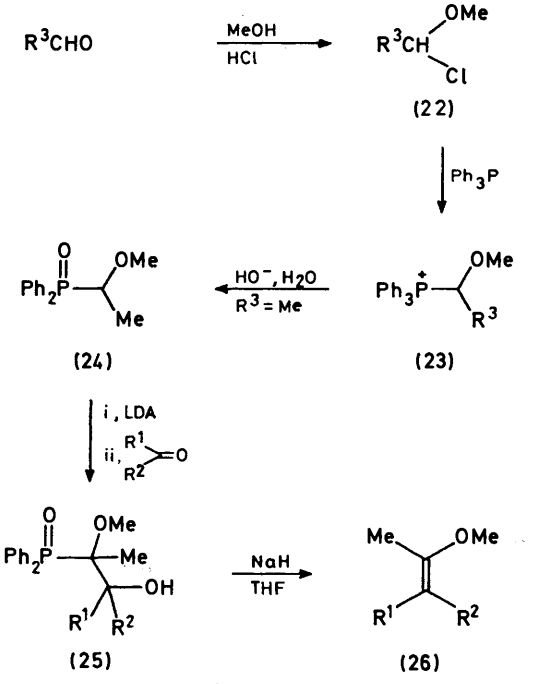
We have recently used [20,21] the reactions of lithium derivatives (13) of alkyldiphenylphosphine oxides (12) with aldehydes to make alcohols (14) which rearrange to the allyl compounds (15) by migration of diphenylphosphinoyl (Ph_2PO) in acid and give normal Horner–Wittig products (16) in base. Yields are high in each step and the alcohols (14) can easily be separated into the two crystalline diastereoisomers, each of which gives a single geometrical isomer of the olefin (16) in base. We now report [22] that the same sequence (12)—(16) with R^2 = OMe can be used to prepare pure samples of each geometrical isomer of a vinyl ether (Schemes 1 and 2). Schlosser [23] has made the vinyl ether from cyclohexanone and the phosphine oxide (18) in 35% yield. Hudrlik [24] has made single isomers of vinyl ethers by stereospecific opening of trimethylsilyl epoxides.



SCHEME 1

Preparation of the Reagents (18) *and* (24).—Diphenyl(methoxymethyl)phosphine oxide (18) can be made in 90% yield * by alkaline hydrolysis of the phosphonium salt (17). Homologues are not so easy to make: the α-chloro-ethers (22) can be made from the corresponding aldehydes by Henry's method [26] and converted into the phosphonium salts (23), but hydrolysis with aqueous base leads to some elimination of triphenylphosphine and we were able to make the phosphine oxide (24) in reasonable yield (60%) only when R^3 = Me.

The Horner–Wittig Reaction.—We normally [21] make the lithium derivatives (13) with butyl-lithium (BuLi) in tetrahydrofuran (THF) but treatment of the α-methoxyalkylphosphine oxides (18) or (24) with BuLi in



SCHEME 2

THF at various temperatures (−78, 0, 25 °C) gave mixtures of products, into some of which butyl groups had been incorporated. However, lithium di-isopropylamide (LDA) at 0 °C gave (19) and the lithium derivative of (24) which were treated with aldehydes or ketones at −78 °C to give adducts (20) and (25) (Tables 1 and 2). Addition at 0 °C or room temperature gave lower yields.

The methoxymethyl compound (18) added equally well to aldehydes or ketones giving mixtures of diastereoisomers of (20). The anisaldehyde adduct (20; R^1 = H, R^2 = *p*-$MeOC_6H_4$) was separated into the two pure crystalline alcohols (27) and (29) (R^2 = *p*-$MeOC_6H_4$, R^3 = H) by column chromatography. The heptaldehyde adduct (20; R^1 = H, R^2 = n-C_6H_{13}) was separated into pure alcohol (27; R^2 = n-C_6H_{13}, R^3 = H) and a 1 : 2 mixture of (27) and (29) (R^2 = n-C_6H_{13}, R^3 = H) by fractional crystallisation from ethyl acetate. The original mixtures contained (27) and (29) in 6 : 5 and

* Trippett [25] reports the same reaction 68% yield.

TABLE 1

Formation of adducts (20) and vinyl ethers (21)

Entry	Temp. of addition (°C)	R^1	R^2	Yield (20) (%)		Yield (21) (%)
1	−78	Et	H	70		
2	−78	n-C_6H_{13}	H	79 [a]	*E*	91
					Z [b]	95
3	room	*p*-$MeOC_6H_4$	H	85 [c]	*E*	88
					Z	70
4	−78	MeCH=CH	H	75		
5	−78	Me	Ph	89		
6	−78	Me	MeCH(OMe)	61		
7	−78	Me	MeCH(SPh)	95 [d]		67
8	room	$[CH_2]_5$		87		55

[a] 1 : 1 Mixture of diastereoisomers. [b] 2 : 1 Mixture of *Z* : *E* isomers. [c] 6 : 5 Mixture of diastereoisomers. [d] Some recovered starting material: 50% conversion.

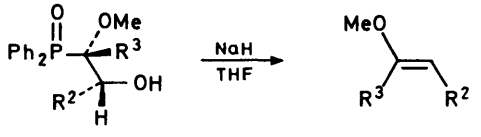
TABLE 2

Formation of adducts (25) and vinyl ethers (26)

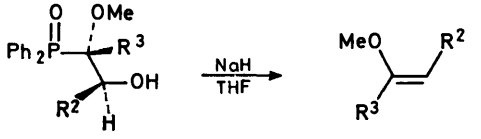
Entry	Temp. of addition (°C)	R^1	R^2	Yield (25) (%)	Yield (26) (%)
1	0	Me	H	57 [28]	
2	−78	Ph	H	88 [28]	
3	−78	*p*-$MeOC_6H_4$	H	75	*E* : 52
					Z : 73
4	−78	Pr^i	H	77 [28]	

1 : 1 ratios respectively, showing there to be little stereoselectivity in the additions of the reagent (19). The α-methoxy-ketone (Entry 6, Table 1) gave a reasonable yield of adduct (61%) but the α-(phenylthio)ketone (Entry 7, Table 1), with a more acidic α proton, gave considerable amounts of starting material and only 50% conversion.

Under the same conditions the methyl-substituted reagent (24) formed a lithium derivative which added well to aldehydes but not to ketones (Table 2). Again, single crystalline diastereoisomers were separated of the anisaldehyde adducts (27) and (29) (R^2 = *p*-$MeOC_6H_4$, R^3 = Me).

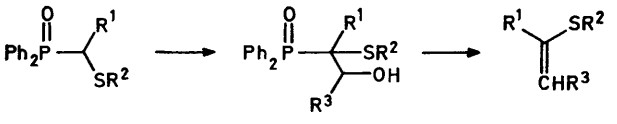


(27) (28)

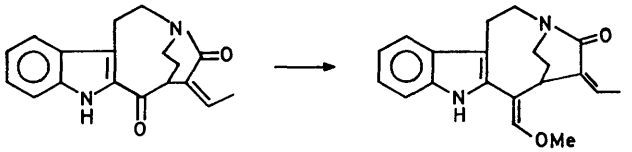


(29) (30)

We have previously reported [27,28] similar reactions with α-(phenylthio)- and α-(methylthio)-alkylphosphine oxides (31; R^2 = Ph, Me). These form anions easily, but addition to aldehydes or ketones then gives the vinyl sulphides (33) directly. Special precautions [28] are needed to isolate the adducts (32). The sulphur atom accelerates the elimination of $Ph_2PO_2^-$ from the anion of (32) whereas the oxygen atom does not accelerate the same reaction on the anions of (20) and (25). This, we believe, is another consequence of the possible destabilisation of carbanions by oxygen atoms in contrast to the stabilisation by sulphur.[27] The reaction (18) to (21) can be carried out in one step by working at a higher temperature (room temperature or above) but yields are usually poorer. Schlosser [23] reports one example of this reaction (same compounds as Entry 8, Table 1) in 35% yield.



(31) (32) (33)



(34) *E* - (35)

The greater reactivity of the methoxy-substituted reagent (19) was an advantage in the conversion of the acyl indole (34) into the vinyl ether (35). The product was needed as an intermediate in syntheses of compounds related to the strychnos alkaloids,[29] and the conjugated ketone (34) failed to react with the ylide (8; R^1 = Me, R^2 = H). The Horner–Wittig reaction with (19) gave a mixture of adducts which were not separated but converted directly by sodium hydride in DMF into a mixture of vinyl ethers (35) separable into geometric isomers by column chromatography.

Completion of the Horner–Wittig Reaction.—Treatment of the adducts (20) or (25) with a sodium base, preferably sodium hydride in THF, at room temperature gave the vinyl ethers (21) or (26) in moderate to excellent yield (Tables 1 and 2). The reaction is stereospecific: each pure diastereoisomer of the anisaldehyde and heptaldehyde adducts (27) and (29); (R^2 = *p*-$MeOC_6H_4$ or C_6H_{13}, R^3 = H or Me) was separately treated with NaH in THF and each gave a single geometrical isomer of the vinyl ether.

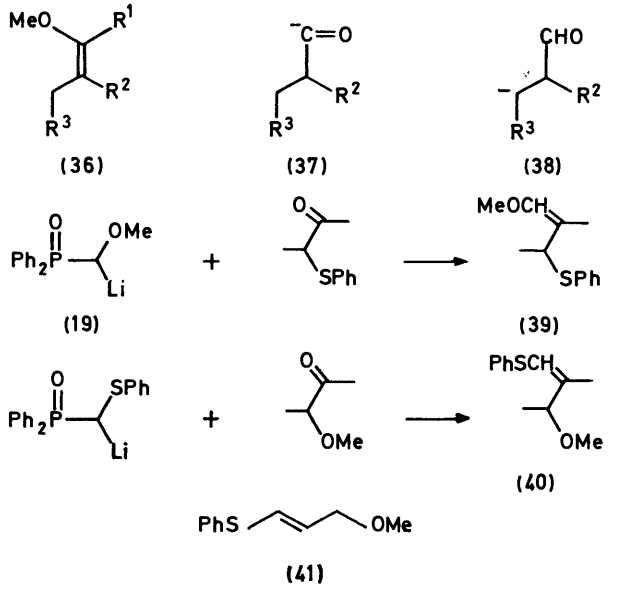
The structures of the vinyl ethers (28) and (30); (R^2 = *p*-$MeOC_6H_4$, R^3 = H) which have two vinyl protons were easily assigned on the basis of their n.m.r. spectra, as the vinyl proton next to oxygen resonates at low field (τ *ca.* 3—4) and the *cis* (7 Hz) and *trans* (13 Hz) coupling constants were clear. We could therefore assign the configurations shown to the alcohols (27) and (29); (R^2 = *p*-$MeOC_6H_4$, R^3 = H). The (*SR,RS*) isomer (27), which gave the *E*-vinyl ether ran faster on t.l.c. ('HR_F isomer'). The n.m.r. spectrum of this diastereoisomer had a higher field *Me*OCP signal and a characteristic shape for the signals of the *ortho* protons in the Ph_2PO group. In most Ph_2PO compounds, including the

(*SR,SR*) isomer (29; $R^2 = p\text{-}MeOC_6H_4$, $R^3 = H$) these protons give one multiplet at slightly lower field than the other protons of the Ph_2PO group, but in the (*SR,RS*) isomer (27; $R^2 = p\text{-}MeOC_6H_4$, $R^3 = H$) two multiplets appear, separated by *ca.* 20 Hz. These are presumably the *ortho* protons of the two diastereotopic phenyl groups.

These characteristic, though not diagnostic, features were reproduced in the n.m.r. spectra of the methyl substituted compounds (27) and (29); ($R^2 = p\text{-}MeOC_6H_4$, $R^3 = Me$) and we therefore assign the (*SR,RS*) configuration (27) to the HR_F isomer and the *E*-geometry to the vinyl ether derived from it. The same features were again found in the n.m.r. spectra of the corresponding sulphur compounds (32) and enabled us to assign configurations to these alcohols and to the vinyl sulphides derived from them.[28] In addition, the reaction to give the vinyl sulphides (33) can be carried out in one step and is then normally stereoselective in favour of the *E*-isomer.[27] The n.m.r. spectra of these vinyl sulphides also conformed to the pattern established for the vinyl ethers.[28]

Only the *E*-isomer (28; $R^2 = n\text{-}C_6H_{13}$, $R^3 = H$) of the vinyl ether from the heptaldehyde adduct could be isolated pure. However, this is the isomer which cannot be made by equilibration of the ' anions ' (2) and (3).

The sequences (18)—(21) and (24)—(26) make single geometrical isomers of vinyl ethers generally available subject to the limitation that the group next to oxygen [R^1 in (36)] may be only H or Me. The most interesting

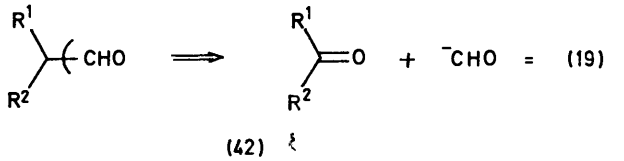


vinyl ethers for synthesis are those with $R^1 = H$ since they can form anions of types (2) or (4), reagents for the synthons (37) and (38), respectively.[5-9]

We also made the phenylthio-substituted vinyl ether (39), as a mixture of isomers, as we had already made [27] its positional isomer (40) from the phenylthio-analogue of (18). The anion of the unsubstituted form of one of these (41) has previously been used in synthesis.[30] Substituted versions can now be made and both compounds (39) and (40) should form anions which act as enone precursors similar to their bis(phenylthio)-analogues.[27,31]

Aldehyde and Ketone Syntheses.—Hydrolysis of vinyl ethers is very simple—a few minutes with aqueous sulphuric acid in THF converts most vinyl ethers quantitatively into the aldehyde or ketone. The sequence (18)—(21) followed by hydrolysis of the vinyl ether is then a reliable aldehyde synthesis, better than that using the sulphur analogue [27] since vinyl sulphides of aldehydes are difficult to hydrolyse. The sulphur analogues provide a better ketone synthesis since they are generally available whereas only the methyl compound (24) is available in the oxygen series. The hydrolysis of vinyl sulphides to ketones, though needing more vigorous conditions than the hydrolysis of vinyl ethers, can be carried out quite easily.[27]

The aldehyde synthesis (18) to (21) is an alkylative transposition on the original carbonyl compound (42) and a synthesis with umpolung,[16] as the reagent (19) is a formyl anion (^-CHO) equivalent.



EXPERIMENTAL

General procedures have been described elsewhere.[21,27]

Methoxymethyldiphenylphosphine Oxide (18).—Triphenylphosphine (48 g) and chloromethyl ether (16.1 g) were heated together in dry benzene (120 ml) at 50 °C for 96 h. The white precipitate of methoxymethyltriphenylphosphonium chloride was collected by filtration and washed with ether to give the phosphonium salt (61 g). This was heated with sodium hydroxide–water (100 ml; 30% w/v), the benzene formed being allowed to distil out of the mixture. When evolution of benzene ceased the mixture was allowed to cool, extracted with chloroform (4 × 30 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The crude product was recrystallised from ethyl acetate to give methoxymethyldiphenylphosphine oxide (40 g, 90%), m.p. 114—116 °C (lit.,[25] 116—117°), R_F (EtOAc) 0.2, τ ($CDCl_3$) 2.0—2.7 (10 H, m, Ph_2PO), 5.81 (2 H, d, J_{PH} 7 Hz, PCH), and 6.58 (3 H, s, OMe).

Methoxyethyldiphenylphosphine Oxide (24).—Similarly, triphenylphosphine (48 g) and chloroethyl methyl ether (18.9 g), heated together in benzene at 50 °C for 50 h gave methoxyethyltriphenylphosphonium chloride (62 g, 97%). Heating with sodium hydroxide–water (30% w/v) gave, after work-up, a very dark red liquid, a portion of which was separated by column chromatography (EtOAc–MeOH as eluant) into triphenylphosphine and *methoxyethyldiphenylphosphine oxide* (24) (12.9 g, equivalent to 60% overall), R_F (EtOAc) 0.15, τ ($CDCl_3$) 1.7—2.7 (10 H, m, Ph_2PO), 5.87 (1 H, quint, $J_{HH} = J_{PH} = 7$ Hz, PC*H*Me), 4.72 (3 H, s, OMe), and 2.55 (3 H, dd, J_{HH} 7, J_{PH} 16 Hz, PCH*Me*).

1-*Diphenylphosphinoyl*-1-*methoxybutan*-2-*ol* (20; $R^1 =$ Et, $R^2 = H$).—Methoxymethyldiphenylphosphine oxide

(1.1 g) in dry THF (30 ml) was stirred with lithium di-isopropylamide (LDA) [from di-isopropylamine (0.8 ml) and n-butyl-lithium (2.2 ml; 2.4M solution in hexane)] in THF (6 ml) at 0 °C for 10 min. The mixture was cooled to −78 °C and propionaldehyde (0.5 ml) in dry THF (5 ml) was added dropwise. The solution was allowed to warm to room temperature and saturated ammonium chloride solution (30 ml) and ether (30 ml) were added. The aqueous layer was extracted with ether (3 × 30 ml), and the combined organic layers dried ($MgSO_4$) and evaporated under reduced pressure to give a clear yellow gum. Column chromatography (ethyl acetate) gave the *HR_F isomer* of the alcohol (20; R^1 = Et, R^2 = H) (632 mg, 46%), m.p. 129—131 °C, R_F (EtOAc) 0.4, τ ($CDCl_3$) 1.8—2.7 (10 H, m, Ph_2PO), 5.6 (1 H, br, OH), 5.8—6.4 (2 H, m, C*H*OMe and C*H*OH), 6.76 (3 H, s, OMe), 8.26 (1 H, d quint, *J* 3 and 8 Hz, CHCH_2*Me), 8.50 (1 H, d, quint, *J* 1 and 8 Hz, CHCH_2*Me), and 9.02 (3 H, t, *J* 8 Hz, CH_2*Me*), *m/e* 303 (*M* − H, 1%), 246 (100), 231 (55), and 201 (Ph_2PO^+, 61) (Found: C, 67.1; H, 6.8; P, 9.9. $C_{17}H_{21}O_3P$ requires C, 67.1; H, 7.0; P, 10.2%), and the *LR_F isomer* (20; R^1 = Et, R^2 = H) (320 mg, 24%), m.p. 110—111 °C, R_F (EtOAc) 0.35, τ ($CDCl_3$) 1.8—2.7 (10 H, m, Ph_2PO), 5.8—6.2 (2 H, m, C*H*OMe and C*H*OH), 6.27 (1 H, br s, OH), 6.73 (3 H, s, OMe), 8.35 (2 H, quint, *J* 7 Hz, CHCH_2Me), and 9.06 (3 H, t, *J* 7 Hz, CH_2*Me*), *m/e* 275 (*M* − Et, 7%), 246 (98), 231 (69), and 202 (Ph_2POH^+, 100) (Found: C, 67.0; H, 7.0; P, 10.0. $C_{17}H_{21}O_3P$ requires C, 67.1; H, 7.0; P, 10.2%).

1-*Diphenylphosphinoyl*-1-*methoxyoctan*-2-*ol* (20; R^1 = n-C_6H_{13}, R^2 = H).—In a similar way methoxymethyldiphenylphosphine oxide (1.1 g), LDA [from n-butyl-lithium (3.5 ml; 1.5M solution in hexane) and di-isopropylamine (0.8 ml) in THF], and *n*-heptaldehyde (0.7 ml) gave a gummy crystalline solid. Column chromatography (EtOAc) gave the *alcohol* (20; R^1 = n-C_6H_{13}, R^2 = H) (1.27 g, 79%) as a mixture of diastereoisomers. Two recrystallisations from ethyl acetate gave one pure isomer (27; R^2 = n-C_6H_{13}, R^3 = H) (346 mg, 22%), m.p. 111—113 °C, R_F (EtOAc) 0.45, τ ($CDCl_3$) 1.8—2.8 (10 H, m, Ph_2PO), 5.4 (0.5 H, br, OH), 5.8—6.4 (2.5 H, m, C*H*OMe, C*H*OH, and remaining OH), 6.72 (3 H, s, OMe), 8.2—9.0 (10 H, m, $[CH_2]_5$), and 9.15 (3 H, t, *J* 5 Hz, CH_2*Me*), *m/e* 361 (*M* + H, 5%), 246 (95), 231 (100), and 202 (Ph_2POH^+, 83) (Found: C, 70.2; H, 8.3; P, 8.6. $C_{21}H_{29}O_3P$ requires C, 70.0; H, 8.1; P, 8.6%), and a 1 : 2 mixture with the other diastereoisomer as a pale yellow gum (920 mg, 57%).

2-*Diphenylphosphinoyl*-2-*methoxy*-1-(p-*methoxyphenyl*)-*ethan*-1-*ol* (20; R^1 = *p*-$MeOC_6H_4$, R^2 = H). Similarly methoxymethyldiphenylphosphine oxide (1.1 g), LDA [from n-butyl-lithium (2.1 ml; 2.4M in hexane) and di-isopropylamine (0.75 ml) in THF], and *p*-anisaldehyde (0.7 ml) gave a gummy crystalline solid which was separated by column chromatography [4 : 1, EtOAc–light petroleum (b.p. 40—60 °C)] into the *HR_F isomer* of the alcohol (27; R^2 = *p*-$MeOC_6H_4$, R^3 = H) (900 mg, 46%), m.p. 124—126 °C, R_F (EtOAc) 0.4, τ ($CDCl_3$) 1.8—2.7 (10 H, m, Ph_2PO), 2.67 (2 H, d, J_{AB} 9 Hz, protons *ortho* to MeO on anisyl ring), 3.18 (2 H, d, J_{AB} 9 Hz, protons *meta* to MeO on anisyl ring), 5.16 (1 H, s, OH), 5.17 (1 H, t, J_{PH} = J_{HH} = 9 Hz, C*H*OH), 6.22 (1 H, dd, J_{PH} 7 and J_{HH} 9 Hz, C*H*OMe), 6.24 (3 H, s, ArO*Me*), and 7.44 (3 H, s, PCOMe), *m/e* 382 (M^+, 0.5%), 364 (10), 246 (89), 231 (100), and 201 (Ph_2PO^+, 48) (Found: C, 69.2; H, 6.2; P, 8.3. $C_{22}H_{23}O_4P$ requires C, 69.1; H, 6.1; P, 8.1%), and the *LR_F isomer* of the alcohol (29; R^2 = *p*-$MeOC_6H_4$, R^3 = H) (750 mg, 39%), m.p. 160—164 °C, R_F (EtOAc) 0.3, τ ($CDCl_3$) 2.0—2.7 (10 H, m, Ph_2PO), 2.72 (2 H, d, J_{AB} 9 Hz, protons *ortho* to MeO on anisyl ring), 3.28 (2 H, d, J_{AB} 9 Hz, protons *meta* to MeO on anisyl ring), 4.75 (1 H, dd, J_{PH} 9 and J_{HH} 3 Hz, C*H*OH), 5.63 (1 H, s, OH), 5.90 (1 H, dd, J_{PH} 2, J_{HH} 3 Hz, CHOMe), 6.27 (3 H, s, ArO*Me*), and 6.95 (3 H, s, PCOMe), *m/e* 383 (*M* + H, 98%), 365 (96), 246 (100), 231 (94), and 201 (Ph_2PO^+, 33) (Found: *M* + H, 383.1406. $C_{22}H_{24}O_4P$ requires *M* + 1, 383.1411).

1-*Diphenylphosphinoyl*-1-*methoxypent*-3-*en*-2-*ol* (20; R^1 = MeCH=CH, R^2 = H).—Similarly, methoxymethyldiphenylphosphine oxide (1.1 g), LDA [from n-butyl-lithium (2.2 ml; 2.4M in hexane) and di-isopropylamine (0.8 ml) in THF at 0 °C], and crotonaldehyde (0.7 ml) at −78 °C gave a brown gum from which the *alcohol* (20; R^1 = MeCH=CH, R^2 = H) was obtained as a mixture of diastereoisomers by column chromatography (EtOAc) (1.1 g, 78%), R_F (EtOAc) 0.23, τ ($CDCl_3$) 1.9—2.7 (10 H, m, Ph_2PO), 3.1—3.7 (2 H, m, C*H*=C*H*), 5.2—5.8 (1 H, m, C*H*OH), 5.62 (1 H, br s, OH), 5.99 and 6.13 (1 H, dd, *J* 4 and 6 Hz, and t, J_{PH} = J_{HH} = 7 Hz, PC*H*), 6.67 and 6.71 (3 H, 2 s, OMe), 2.41—2.54 (3 H, 2 d, *J* 5 or 8 Hz, CH*Me*), *m/e* 317 (*M* + H, 1%), 275 (2), 259 (2), 246 (100), 231 (98). and 201 (Ph_2PO^+, 56) (Found: M^+, 316.1238. $C_{18}H_{21}O_3P$ requires *M*, 316.1229).

1-*Diphenylphosphinoyl*-1-*methoxy*-2-*phenylpropan*-2-*ol* (20; R^1 = Me, R^2 = Ph).—In the same way methoxymethyldiphenylphosphine oxide (1.1 g), LDA [from n-butyl-lithium (3.5 ml; 1.5M solution in hexane) and di-isopropylamine (0.8 ml) in THF], and acetophenone (in THF saturated with anhydrous lithium bromide) at −78 °C gave a yellow gum which was purified by column chromatography (EtOAc) to give a total yield of (1.45 g, 89%) of alcohol (20; R^1 = Me, R^2 = Ph) as a 1 : 1 mixture (n.m.r.) of diastereoisomers. These were separated partially on the column giving the *HR_F isomer* (402 mg, 25%), m.p 159—160 °C, R_F (EtOAc) 0.55, τ ($CDCl_3$) 1.8—2.9 (15 H, m, Ph_2PO and Ph), 4.38 (1 H, s, OH), 6.09 (1 H, d, J_{PH} 6 Hz, C*H*OMe), 7.39 (3 H, s, OMe), and 8.37 (3 H, s, OMe), *m/e* 367 (*M* + H, <1%), 246 (100), 231 (81), and 201 (Ph_2PO^+, 17) (Found: C, 71.9; H, 6.3; P, 8.2. $C_{22}H_{23}O_3P$ requires C, 72.1; H, 6.3; P, 8.5%), and the *LR_F isomer* (180 mg, 11%), m.p. 147—149 °C, R_F (EtOAc) 0.50, τ ($CDCl_3$) 2.0—3.2 (15 H, m, Ph_2PO and Ph), 4.51 (1 H, br s, OH), 5.80 (1 H, d, J_{PH} 6 Hz, C*H*OMe), 6.74 (3 H, s, OMe), and 8.33 (3 H, s, CMe), *m/e* 367 (*M* + H, 0.5%), 348 (5), 246 (86), 231 (100), and 201 (Ph_2PO^+, 20) (Found: C, 72.2; H, 6.4; P, 8.7. $C_{22}H_{23}O_3P$ requires C, 72.1; H, 6.3; P, 8.5%), together with a mixture of the two isomers (863 mg, 53%).

1-*Diphenylphosphinoyl*-1,3-*dimethoxy*-2-*methylbutan*-2-*ol* [20; R^1 = Me, R^2 = MeCH(OMe)].—In the same way methoxymethyldiphenylphosphine oxide (1.1 g), LDA [from n-butyl-lithium (2.5 ml; 2.4M solution in hexane) and di-isopropylamine (0.8 ml) in THF], and 3-methoxybutan-2-one (650 mg) at −78 °C gave, after the usual work-up followed by column chromatography (EtOAc), a mixture of *two diastereoisomers* of the alcohol [20; R^1 = Me, R^2 = MeCH(OMe)] (489 mg, 31%), m.p. 111—130 °C, R_F (EtOAc) 0.3, τ ($CDCl_3$) 1.9—2.7 (10 H, m, Ph_2PO), 5.59 (1 H, s, OH), 5.78 and 5.82 (1 H, 2 s, PC*H*OMe), 6.39 and 6.57 (1 H, 2 q, *J* 6 Hz, C*H*Me), 6.82, 6.95, 7.00, and 7.13 [6 H, 4 s, POCMe and C(Me)O*Me*], 8.83 and 8.89 (3 H, 2 s, CMe), and 8.86 (3 H, 2 d, *J* 6 Hz, CH*Me*), *m/e* 349 (*M* + H, 6%), 315 (8), 301 (11), 289 (62), 246 (65), 231 (57), and 201 (Ph_2PO^+, 100) (Found: C, 65.8; H, 7.2; P, 8.6. $C_{19}H_{25}O_4P$ requires

C, 65.5; H, 7.2; P, 8.9%), a mixture of the *two other diastereoisomers* (190 mg, 12%), m.p. 90—125 °C, R_F (EtOAc) 0.25, τ ($CDCl_3$) 1.6—2.7 (10 H, m, Ph_2PO), 5.42 and 5.77 (1 H, 2 d, J_{PH} 4 and 8 Hz respectively, PCH), 5.88 (1 H, s, OH), 6.15 and 6.36 (1 H, 2 q, J 6 Hz, C*H*Me), 6.65, 6.75, 6.79, and 6.89 [6 H, 4 s, PCO*Me* and C(Me)O*Me*], 8.78 and 8.89 (3 H, 2 d, J 6 Hz, CH*Me*), and 8.90 and 8.92 (3 H, 2 s, CMe), *m/e* 349 (M + H, 13%), 301 (10), 289 (42), 246 (68), 231 (63), and 201 (Ph_2PO^+, 100) (Found: M + H, 349.1558. $C_{19}H_{26}O_4P$ requires M + 1, 349.1569), and a mixture of all four diastereoisomers (274 mg, 18%).

1-*Diphenylphosphinoyl*-1-*methoxy*-2-*methyl*-3-*phenylthiobutan*-2-*ol* [20; R^1 = Me, R^2 = MeCH(SPh)].—Similarly, methoxymethyldiphenylphosphine oxide (1.1 g), LDA [from n-butyl-lithium (2.2 ml; 2.4M solution in hexane), and di-isopropylamine (0.8 ml) in THF], and 3-phenylthiobutan-2-one [32] (1 g) gave a pale yellow oil. Preparative t.l.c. (EtOAc as eluant) of a portion gave starting phosphine oxide (60 mg, equivalent to 50% overall) and the alcohol [20; R^1 = Me, R^2 = MeCH(SPh)] (100 mg, equivalent to 47.5% overall), this representing a 95% yield based on unrecovered starting material. Column chromatography [1 : 1 EtOAc–light petroleum (b.p. 40—60 °C) as eluant] gave a mixture of *three diastereoisomers* of the alcohol as gummy crystals (350 mg, 18%), R_F (EtOAc) 0.55, τ ($CDCl_3$) 1.7—3.0 (15 H, m, Ph_2PO and PhS), 5.08, 5.29, and 5.48 (1 H, 3 d, J_{PH} 4, 8, and 3 Hz respectively, C*H*OMe), 4.9—5.6 (1 H, br, OH), 5.77, 6.34, and 6.41 (1H, 3 q, J_{HH} all 7 Hz, C*H*Me) 6.76, 6.80, and 6.86 (3 H, 3 s, OMe), 8.56, 8.74, and 8.77 (3 H, 3 d, J_{HH} all 7 Hz, CH*Me*), and 8.60 (3 H, s, CMe), and one *pure diastereoisomer* (125 mg, 7%), m.p. 138—140 °C, R_F (EtOAc) 0.5, τ ($CDCl_3$) 1.9—3.0 (15 H, m, Ph_2PO and PhS), 5.3 (1 H, br OH), 5.54 (1 H, s, C*H*OMe), 6.13 (1 H, q, J 7 Hz, C*H*Me), 7.04 (3 H, s, OMe), 8.59 (3 H, d, J 7 Hz, CH*Me*), and 8.76 (3 H, s, CMe), *m/e* 299 (M − PhS − H_2O, 7%), 289 (36), 246 (19), 231 (22), and 201 (Ph_2PO^+, 100) (Found: C, 67.7; H, 6.6; P, 7.1. $C_{24}H_{27}O_2PS$ requires C, 67.6; H, 6.4; P, 7.3%), together with a mixture of all four isomers (187 mg, 10%).

1-(*Diphenylphosphinoylmethoxymethyl*)*cyclohexan*-1-*ol* (20; R^1R^2 = −$[CH_2]_5$−).—In the same way, methoxymethyldiphenylphosphine oxide (1.1 g), LDA [from n-butyl-lithium (2.1 ml; 2.4M solution in hexane) and di-isopropylamine (0.75 ml) in THF], and cyclohexanone (0.75 ml) gave a pale yellow solid. Recrystallisation from EtOAc gave the alcohol (20; R^1R^2 = −$[CH_2]_5$−) (1.32 g, 87%), m.p. 134—136 °C, R_F (EtOAc) 0.4, τ ($CDCl_3$) 1.7—2.7 (10 H, m, Ph_2PO), 5.59 (1 H, s, OH), 6.21 (1 H, d, J_{PH} 6 Hz, PCH), 6.80 (3 H, s, OMe), and 8.0—9.0 (10 H, m, $[CH_2]_5$ of ring), *m/e* 345 (M + H, 13%), 344 (M^+, 14), 331 (28), 246 (100), 231 (91), and 201 (Ph_2PO^+, 62) (Found: C, 69.7; H, 7.5; P, 8.8. $C_{20}H_{25}O_3P$ requires C, 69.8; H, 7.3; P, 9.0%).

2-*Diphenylphosphinoyl*-2-*methoxy*-1-(p-*methoxyphenyl*)-*propan*-1-*ol* (25; R^1 = *p*-$MeOC_6H_4$, R^2 = H).—Similarly, 1-methoxyethyldiphenylphosphine oxide (1.25 g), LDA [from n-butyl-lithium (2.2 ml; 2.4M in hexane) and di-isopropylamine (0.8 ml) in THF], and anisaldehyde (0.7 ml) at −78 °C gave a yellow solid which was separated into the HR_F *isomer* of the alcohol (25; R^1 = *p*-$MeOC_6H_4$, R^2 = H) (940 mg, 49%), m.p. 133—135 °C, R_F (EtOAc) 0.4, τ ($CDCl_3$) 1.7—2.7 (10 H, m, Ph_2PO), 2.72 (2 H, d, J_{AB} 9 Hz, protons *ortho* to MeO on anisyl ring), 3.20 (2 H, d, J_{AB} 9 Hz, protons *meta* to MeO on anisyl ring), 4.97 (1 H, s, OH), 5.03 (1 H, d, J_{PH} 10 Hz, C*H*OH), 6.25 (3 H, s, ArO*Me*), 7.30 (3 H, s, PCOMe), and 8.60 (3 H, d, J_{PH} 16 Hz, PCMe), *m/e* 378 (M − H_2O, 14%), 260 (100), 245 (100), and 202 (Ph_2POH^+, 79) (Found: M − H_2O, 378.1385. $C_{23}H_{23}O_3P$ requires M − 18, 378.1385), and the LR_F *isomer* (503 mg, 26%), m.p. 184—186 °C [from $CHCl_3$–light petroleum (b.p. 60—80 °C)], R_F (EtOAc) 0.25, τ ($CDCl_3$) 2.0—2.8 (10 H, m, Ph_2PO), 2.80 (2 H, d, J_{AB} 9 Hz, protons *ortho* to MeO on anisyl ring), 3.41 (2 H, d, J_{AB} 9 Hz, protons *meta* to MeO on anisyl ring), 5.02 (1 H, d, J_{PH} 13 Hz, C*H*OH), 5.52 (1 H, s, OH), 6.31 (3 H, s, ArO*Me*), 6.64 (3 H, s, PCOMe), and 8.56 (3 H, d, J_{PH} 15 Hz, PCMe), *m/e* 397 (M − H, 10%), 378 (23), 260 (98), 245 (100), and 202 (Ph_2POH^+, 81) (Found: C, 69.9; H, 6.5; P, 8.0. $C_{23}H_{25}O_4P$ requires C, 69.7; H, 6.4; P, 7.8%).

Vinyl Ethers.—Most of the vinyl ethers have been reported before as mixtures of geometrical isomers or as compounds of undefined geometry. These quoted sources give analytical data. We give only additional data characteristic of each single geometrical isomer.

(E)-1-*Methoxyoct*-1-*ene* * (28; R^2 = n-C_6H_{13}, R^3 = H). The alcohol (27; R^2 = n-C_6H_{13}, R^3 = H) (400 mg; one pure isomer obtained by crystallisation) was dissolved in dry THF (25 ml) and stirred with sodium hydride [120 mg; 50% dispersion in oil, washed with dry light petroleum (b.p. 30—40 °C)] for 22 h. The mixture was filtered through Hyflo to remove the gelatinous precipitate of sodium diphenylphosphinite, the residue washed with ether, and the combined organic fractions evaporated under reduced pressure at room temperature to give (*E*)-1-methoxyoct-1-ene (28; R^2 = n-C_6H_{13}, R^3 = H) (144 mg, 91%) as a colourless liquid, R_F (EtOAc) 0.8, $\nu_{max.}$ (film) 2 930 (C–H), 1 665 (C=C), and 940 cm^{-1} (*E*-C=C), τ ($CDCl_3$) 3.82 (1 H, dt, J 13 and 1 Hz, C*H*OMe), 5.42 (1 H, dt, J 13 and 7 Hz, C*H*=CHOMe), 6.58 (3 H, s, OMe), 8.11 (2 H, br q, J 7 Hz, CH_2CH=CH), 8.5—8.9 (8 H, br, $[CH_2]_4$Me), and 9.10 (3 H, t, J 6 Hz, CH_2*Me*).

(Z)-1-*Methoxyoct*-1-*ene* * (*in a mixture of geometrical isomers*) (21; R^1 = H, R^2 = n-C_6H_{13}). The alcohol (20; R^1 = n-C_6H_{13}, R^2 = H) (920 mg, a mixture of diastereoisomers left by the recrystallisation of one pure isomer) in THF (40 ml), stirred with sodium hydride (300 mg; 50% dispersion in oil) for 24 h, gave, in the same way as above, a mixture of geometrical isomers (2 : 1, *Z* : *E*) of the vinyl ether (21; R^1 = H, R^2 = n-C_6H_{13}) (440 mg, 95%), R_F (EtOAc) 0.7, $\nu_{max.}$ (liquid film) 2 930 (C–H) and 1 670 cm^{-1} (C=C). By comparison with the n.m.r. spectrum of the pure *E*-isomer, the *Z*-isomer showed τ ($CDCl_3$) 4.26 (1 H, dt, J 6 and 1 Hz, C*H*OMe), 5.78 (1 H, q, J 6 Hz, CH=CHOMe), 6.51 (3 H, s, OMe), 7.6—8.3 (2 H, m, CH_2CH=CH), 8.4—8.9 (8 H, broad, $[CH_2]_4$Me), and 9.12 (3 H, t, J 6 Hz, CH_2*Me*).

(E)-1-(p-*Methoxyphenyl*)-2-*methoxyethylene* (28; R^2 = *p*-$MeOC_6H_4$, R^3 = H). Similarly, the HR_F isomer of the alcohol (27; R^2 = *p*-$MeOC_6H_4$, R^3 = H) (450 mg), stirred in THF with sodium hydride (120 mg; 50% dispersion in oil) for 18 h, gave a yellow liquid. Distillation under reduced pressure gave, on cooling in air, white crystals of the *E*-isomer of the vinyl ether (28; R^2 = *p*-$MeOC_6H_4$, R^3 = H) (170 mg, 88%), b.p. 100—116 °C at 18 mmHg (lit.,[33] 120—126 °C at 14 mmHg), R_F (EtOAc) 0.7, τ ($CDCl_3$) 2.98 (2 H, d, J_{AB} 9 Hz, protons *ortho* to MeO on anisyl ring), 3.19 (1 H, d, J_{trans} 13 Hz, C*H*OMe), 3.32 (2 H, d, J_{AB} 9 Hz, protons *meta* to MeO on anisyl ring), 4.35 (1 H, d, J_{trans} 13 Hz, C*H*Ar), 6.33 (3 H, s, ArO*Me*), and 6.45 (3 H, s, PCOMe), *m/e* 164 (M^+, 100%), 149 (63), 135 (27), and 121 (95).

* Each isomer of this compound has been made by Hudrlik.[24]

(Z)-1-(*Methoxyphenyl*)-2-*methoxyethylene* (30; R^2 = *p*-$MeOC_6H_4$, R^3 = H). By a similar procedure the LR_F isomer of the alcohol (29; R^2 = *p*-$MeOC_6H_4$, R^3 = H) (400 mg) stirred with sodium hydride (120 mg; 50% dispersion in oil) in THF (20 ml) for 18 h gave a liquid which was distilled under reduced pressure to give the *Z*-isomer of the vinyl ether (30; R^2 = *p*-$MeOC_6H_4$, R^3 = H) (120 mg, 70%), b.p. 100—120 °C at 19 mmHg (lit.,[33] 120—126 °C at 14 mmHg), R_F (EtOAc) 0.7, $\nu_{max.}$ ($CHCl_3$ 1 660 (C=O), 1 610, 1 574, and 1 511 (Ar), 1 248 and 1 032 (C–O), and 840 cm^{-1} (Ar), τ ($CDCl_3$) 2.60 (2 H, d, J_{AB} 9 Hz, protons *ortho* to MeO on anisyl ring), 3.28 (2 H, d, J_{AB} 9 Hz, protons *meta* to MeO on anisyl ring), 4.08 (1 H, d, J_{cis} 7 Hz, C*H*OMe), 4.92 (1 H, d, J_{cis} 7 Hz, C*H*Ar), 6.28 (3 H, s, ArO*Me*), and 6.32 (3 H, s, PCOMe), *m/e* 164 (M^+, 100%), 149 (64), and 121 (56).

1-*Methoxy*-2-*methyl*-3-*phenylthiobut*-1-*ene* [21; R^1 = Me, R^2 = MeCH(SPh)]. A mixture of the four diastereoisomers of the alcohol [20; R^1 = Me, R^2 = MeCH(SPh)] (180 mg) was stirred with sodium hydride (60 mg; 50% dispersion in oil) in THF for 5 h and gave, in a similar way to the above, a pale yellow oil. Preparative t.l.c. (EtOAc as eluant) gave the *vinyl ether* [21; R^1 = Me, R^2 = MeCH(SPh)] as a 3 : 5 mixture (n.m.r.) of geometrical isomers (61 mg, 67%), R_F (EtOAc) 0.7, τ ($CDCl_3$) (major isomer) 2.5—2.9 (5 H, m, PhS), 4.36 (1 H, q, $J_{allylic}$ 2 Hz, C*H*OMe), 5.36 (1 H, q, *J* 7 Hz, C*H*Me), 6.64 (3 H, s, OMe), 8.44 (3 H) d, $J_{allylic}$ 2 Hz, CH=C*Me*), 8.66 (3 H, d, *J* 7 Hz, CH*Me*), and (minor isomer) 2.5—2.9 (5 H, m, PhS), 4.43 (1 H, q, $J_{allylic}$ 2 Hz, C*H*OMe), 6.42 (1 H. q, *J* 7 Hz, C*H*Me), 6.61 (3 H, s, OMe), 8.36 (3 H, d, $J_{allylic}$ 2 Hz, C*H*=CMe), and 8.62 (3 H, d, *J* 7 Hz, CH*Me*), *m/e* 208 (M^+, 5%), 193 (17), 180 (50), 179 (42), 110 (58), and 99 (*M* — PhS, 100).

Cyclohexylidenylmethyl methyl ether (21; R^1R^2 = $-[CH_2]_5-$). In the same way, the alcohol (20; R^1R^2 = $-[CH_2]_5-$] (500 mg) and sodium hydride (120 mg; 60% suspension in oil) in dry THF (20 ml) gave, after stirring together for 45 h followed by the usual work-up, a liquid which was distilled under reduced pressure to give the vinyl ether[23] (21; R^1R^2 = $-[CH_2]_5-$) (100 mg, 55%), b.p. 50—60 °C at 18 mmHg (lit.,[12] 74 °C at 48 mmHg), R_F (EtOAc) 0.7, $\nu_{max.}$ (liquid film) 2 930 (C–H), 1 690 (C=C), and 1 260 cm^{-1} (C–O), τ ($CDCl_3$) 4.38 (1 H, s + fine allylic coupling, C*H*OMe), 6.54 (3 H, s, OMe), 7.80—7.96 and 8.02—8.20 [2 H, each, 2 m, CH_2C(=CHOMe)CH_2], and 8.3—8.6 (6 H, m, remaining $-[CH_2]_3-$ of ring).

(E)-1-(p-*Methoxyphenyl*)-2-*methoxyprop*-1-*ene* (30; R^2 = *p*-$MeOC_6H_4$, R^3 = Me). Treatment of the HR_F isomer of the alcohol (29; R^2 = *p*-$MeOC_6H_4$, R^3 = Me) (450 mg) in THF with sodium hydride (120 mg; 50% dispersion in oil) gave, in the same way as above, the vinyl ether * (30; R^2 = *p*-$MeOC_6H_4$, R^3 = Me) as a colourless liquid (120 mg, 52%), R_F (EtOAc) 0.7, τ ($CDCl_3$) 3.04 (2 H, d, J_{AB} 9 Hz, protons *ortho* to MeO on anisyl ring), 3.30 (2 H, d, J_{AB} 9 Hz, protons *meta* to MeO on anisyl ring), 4.58 (1 H, s, ArC*H*), 6.25 (3 H, s, ArO*Me*), 6.42 (3 H, s, MeCO*Me*), and 8.10 (3 H, s, CMe), *m/e* 178 (M^+, 100%), 163 (64), and 135 (39).

(Z)-1-(p-*Methoxyphenyl*)-2-*methoxyprop*-1-*ene* (30; R^2 = *p*-$MeOC_6H_4$, R^3 = Me). In the same way, treatment of the LR_F isomer of the alcohol (29; R^2 = *p*-$MeOC_6H_4$, R^3 = Me) (300 mg) with sodium hydride (100 mg; 50% dispersion in oil) in THF for 4 h gave the vinyl ether * (30; R^2 = *p*-$MeOC_6H_4$, R^3 = Me) as a pale yellow liquid (112 mg, 73%), R_F (EtOAc) 0.7, τ ($CDCl_3$) 2.67 (2 H, d, J_{AB} 9 Hz, protons *ortho* to MeO on anisyl ring), 3.34 (2 H, d, J_{AB} 9 Hz, protons *meta* to MeO on anisyl ring), 4.84 (1 H, s, C=CH), 6.33 (3 H, s, ArO*Me*), 6.41 (3 H, s, MeCO*Me*), and 8.07 (3 H, s, CMe), *m/e* 179 (*M* + H, 36%), 164 (50), 135 (30), and 121 (100).

5-*Ethylidene*-(Z)-4-*oxo*-7-*methoxymethylene*-1,4,5,6,7,8-*hexahydro*-2H-3,6-*ethanoazonino*[5,4-b]*indole* (35).—To a solution of methoxymethyldiphenyl phosphine oxide (18) (393.6 mg, 1.6mM) in dry THF (15 ml) at −5 °C, under nitrogen, was added a solution in hexane of n-butyllithium (0.84 ml; 1.67M; 1.4mM). After stirring for 5 min the acyl indole (34) (117.6 mgs, 0.4mM) in dry THF (15 ml) was added. Stirring was continued for a further 30 min. The mixture was poured into saturated aqueous ammonium chloride (40 ml) and the solution extracted with ethyl acetate (3 × 25 ml). The combined organic extracts were dried (Na_2SO_4) and evaporated to give a colourless gum.

The crude product was dissolved in dry DMF (10 ml) and sodium hydride (40 mg, 50% dispersion in oil) added over 5 min with stirring. After a further 15 min the mixture was poured into saturated sodium chloride solution (50 ml) and extracted with ethyl acetate (3 × 25 ml). The combined organic extracts were dried (Na_2SO_4) and evaporated to give a dark orange gum. The product was purified by short-path column chromatography on silica gel (Whatman SOTLC, 20 gm). Elution with ethyl acetate–light petroleum (b.p. 60—80°) (3 : 2) gave two components (89 mg, 69%).

The less polar *vinyl ether* (*E*)-(35) (52 mg) was recrystallised from dichloromethane–hexane and had m.p. 214—216 °C, R_F 0.51 (EtOAc), $\nu_{max.}$ 3 460 (NH), 1 675 (C=C), 1 650 (C=O), and 1 620 cm^{-1} (amide), $\lambda_{max.}$ 225, 285, and 293 nm, τ (CDCl) 1.88 (1 H, s, NH), 2.4—3.1 (4 H, m, ArH), 3.96 (1 H, d, *J* 2 Hz, C=C*H*OMe), 4.22 (1 H, q, *J* 7 Hz, C=C*H*Me), 6.42 (3 H, s, OMe), and 8.06 (3 H, d, *J* 7 Hz, C=CH*Me*), *m/e* 322 (M^+) (Found: C, 74.2; H, 6.9; N, 8.7. $C_{20}H_{22}N_2O_3$ requires C, 74.5; H, 6.8; N, 8.7%).

The more polar *vinyl ether* (*Z*)-(35) (37 mg) was recrystallised from dichloromethane–hexane and had m.p. 230—232 °C, R_F 0.32 (EtOAc), $\nu_{max.}$ 3 470 (NH), 1 670 (C=C) 1 650 (C=C), and 1 625 cm^{-1} (amide), $\lambda_{max.}$ 225, 286, and 295 nm, τ ($CDCl_3$) 1.72 (1 H, s, NH), 2.2—3.2 (4 H, m, ArH), 3.78 (1 H, d, *J* 2 Hz, C*H*OMe), 4.36 (1 H, q, *J* 7 Hz, C=C*H*Me), 6.62 (3 H, s, OMe), and 8.14 (3 H, d, *J* 7 Hz, C=CH*Me*), *m/e* 322 (M^+) (Found: C, 74.4; H, 6.9; N, 8.6. $C_{20}H_{22}N_2O_3$ requires C, 74.5; H, 6.8; N, 8.7%).

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* The compounds '$OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}C(OMe){:}CH_2$' described by Daufresne[34] and '$OMe{\cdot}C_6H_4{\cdot}CMe{:}CHOMe$' described by Tiffeneau[35] are almost certainly both mixtures of geometrical isomers of this vinyl ether (30; $R^{1,2}$ = *p*-$MeOC_6H_4-$, Me). In view of the old controversy[34,36] about the structures of these compounds and their hydrolysis products, we hydrolysed (dilute H_2SO_4 in THF) both vinyl ethers. The only product was *p*-methoxyphenylacetone.

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