Photochemical Addition of Methanol to Stilbenes

Jan Woning, Albert Oudenampsen, and Wim H. Laarhoven *
Department of Organic Chemistry, Catholic University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

The photochemical addition of methanol to the alkenic bond of stilbene (**1**) involves two competitive pathways: *viz.* either direct addition of methanol to the alkenic bond or insertion by methanol of a carbene (**13**), emerging from a 1,2-H shift in (**1**). From the observed effect of substituents and the wavelength on the rates of these processes, the rearrangement pathway was concluded to involve excited (**1**) in a vibrationally unrelaxed S_1-state. The direct pathway might involve either a planar ($\pi\pi^*$) or a twisted excited S_1-state of (**1**). The available experimental evidence precludes zwitterionic excited states from being involved in both pathways. The photochemical addition of methanol to the alkenic bond of 1,1-diphenylethene (**3**) follows a similar course. In this case a 1,2-Ph shift in excited (**3**) gives rise to carbene (**13**) and its insertion products.

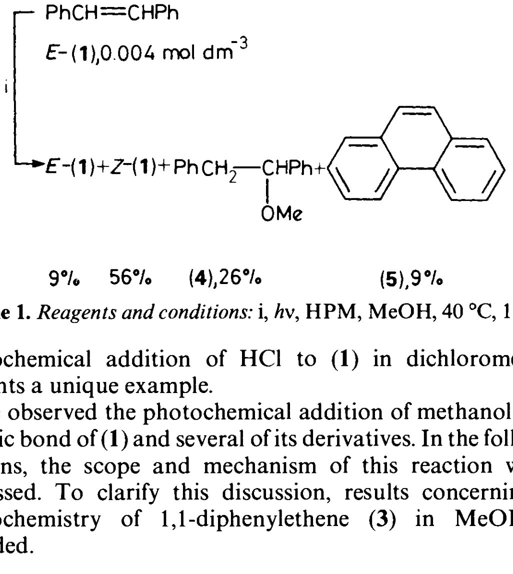
The photochemistry of stilbene (**1**) has been the subject of detailed studies for many years. *E,Z*-isomerization (from either the lowest excited singlet or triplet state)[1] of *E*- and *Z*-(**1**) and conrotatory electrocyclic ring closure of *Z*-(**1**) (from the S_1 state) to 4*a*,4*b*-dihydrophenanthrene[2] were established as the most efficient photoprocesses. Exciplex formation of excited *E*-(**1**) with secondary[3] or tertiary[4] amines presents a relatively new aspect of stilbene photochemistry.

In addition to *E,Z*-isomerization and electrocyclization, many aspects of the photochemistry (*e.g.* dimerization, [2 + 2] and [4 + 2] cycloadditions) of styrenes and non-aromatic alkenes,[5] have been observed with (**1**) and its derivatives. However, photochemical addition of solvents like H_2O, MeOH, and EtOH (compounds containing σ-bonds only) to the alkenic bond of (**1**) itself, has not been described.[6]

This type of addition is well known for aliphatic alkenes and styrenes. In these cases the addition of an alcohol can occur by different mechanisms, *viz.* (*i*) by nucleophilic attack on a Rydberg π,R(3s) excited state;[5] (*ii*) by protonation of the S_1 state. McEwen[7] demonstrated the photochemical addition of water to styrenes and phenylacetylenes to be subject to general acid catalysis; (*iii*) *via* a carbene intermediate, arising from a Rydberg π,R(3s) or a π,π^* excited state of the alkene.[5,8]

With stilbene derivatives, such photochemical addition reactions have only been observed in a few, exceptional cases. Thus, the occurrence of photochemical addition of methanol to the alkenic double bond is known only for 1,2-diphenylcyclobutene,[9] a strained derivative of (**1**) and the charged 4,4′-ethene-1,2-diylbis(1-methylpyridinium) ion.[10] The former compound is exceptional in that neither *E,Z*-isomerization nor electrocyclization to the corresponding 4a,4b-dihydrophenanthrene can occur. On the basis of an observed catalytic effect of acids on the rate of methanol addition and the results of irradiations in MeOD and D_2O, it was concluded[9] that the S_1 state of 1,2-diphenylcyclobutene is deactivated through protonation by these solvents. Besides addition of methanol to the alkenic bond, rearrangement of the resulting carbenium ion takes place.

The 4,4′-ethene-1,2-diylbis(1-methylpyridinium) salts are exceptional in that their S_1 states are said[10] to be electron-deficient at the alkenic positions and hence, prone to be trapped by the addition of nucleophiles to the alkenic bond. It has been stated that photochemical addition of methanol to the alkenic bond of unstrained 1,2-diphenylcyclopentene (**2**)[9] and (**1**) itself[6] does not take place. In this context, the recently reported[11] photochemical addition of HCl to (**1**) in dichloromethane presents a unique example.

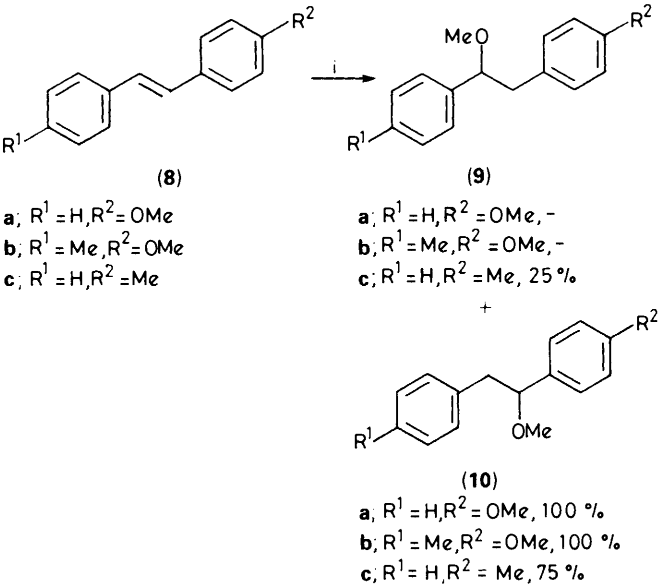


Scheme 1. *Reagents and conditions:* i, *hv*, HPM, MeOH, 40 °C, 135 min.

We observed the photochemical addition of methanol to the alkenic bond of (**1**) and several of its derivatives. In the following sections, the scope and mechanism of this reaction will be discussed. To clarify this discussion, results concerning the photochemistry of 1,1-diphenylethene (**3**) in MeOH are included.

Results and Discussion

Scope of the Reaction.—As part of a continuous research programme aimed at the elucidation of the structure–reactivity relation concerning the primary photocyclization of *Z*-stilbenes to the corresponding 4*a*,4*b*-dihydrophenanthrenes and the effect of solvents thereupon,[12] *E*-(**1**) was irradiated in MeOH under strictly anaerobic conditions. In the ^{1}H n.m.r. spectrum of the resulting mixture of photoproducts, the occurrence of a sharp singlet at δ 3.18, attributable to the presence of a methyl ether, was noted. Chromatographic separation afforded a non-polar fraction [containing (**1**) and phenanthrene] and a polar fraction consisting of a single component (g.l.c.). The ^{1}H n.m.r. and mass spectrum of the latter were assigned to 1-methoxy-1,2-diphenylethane [α-methoxybibenzyl, (**4**)], the methanol adduct of (**1**) (Scheme 1). This assignment was confirmed by chemical synthesis of (**4**).[13] Preliminary results indicate the photochemical addition of MeOH to the alkenic bond to be a general reaction of stilbene derivatives. The reaction depicted in Scheme 1 has been performed successfully with several stilbene derivatives, *e.g.* 1,2-diphenylcyclopentene (**2**), 3-phenyl-1,2-dihydronaphthalene,[14] and the symmetrically substituted 3,3′-dimethyl- (**6**) and 4,4′-difluoro-stilbene [(**7**),



(8)
a; $R^1 = H, R^2 = OMe$
b; $R^1 = Me, R^2 = OMe$
c; $R^1 = H, R^2 = Me$

(9)
a; $R^1 = H, R^2 = OMe$, -
b; $R^1 = Me, R^2 = OMe$, -
c; $R^1 = H, R^2 = Me$, 25 %
+

(10)
a; $R^1 = H, R^2 = OMe$, 100 %
b; $R^1 = Me, R^2 = OMe$, 100 %
c; $R^1 = H, R^2 = Me$, 75 %

Scheme 2. *Reagents and conditions:* i, 300 nm, MeOH.

Scheme 2, $R^1 = R^2 = F$]. In case of the asymmetrically substituted 4-methoxy-(**8a**) and 4-methoxy-4′-methylstilbene (**8b**) addition of MeOH was observed to occur regioselectively, affording the methanol adducts (**10a**) and (**10b**) respectively, in accordance with Markovnikov's rule (Scheme 2). The position of the methoxy group, relative to that of the substituents R was deduced from the c.i. mass spectra, in which the presence of an intense fragmentation peak at m/z 151 due to a $MeOC_6H_4CHOMe^+$ fragment is consistent with structures (**10a, b**) rather than with (**9a, b**). The assignment of structure (**10a**) to the methanol adduct of 4-methoxystilbene (**8a**) was subsequently verified by chemical synthesis of the regioisomeric α- and β-methoxy(4-methoxy)bibenzyls (**9a**) and (**10a**). As indicated in Scheme 2, the photochemical addition of MeOH to (**8c**) does not take place with 100% regioselectivity, though in this case too, the Markovnikov adduct α-methoxy(4-methyl)-bibenzyl (**10c**) predominates.

For *trans*-stilbene [*E*-(**1**)] the progress of the photoreaction has been monitored as a function of the irradiation time. The resulting yield *vs.* time curves for conversion of *E*-(**1**) and formation of *Z*-(**1**), phenanthrene (**5**) and the methanol adduct (**4**) are presented in Figure 1. Obviously (**4**) is a primary photoproduct, since its yield *vs.* time curve intercepts at the origin. From the observation that the photostationary *Z*-(**1**):*E*-(**1**) ratio of 6.5 is reached within 2 min and the magnitude of the slope of the yield *vs.* time curve of methanol adduct (**4**), it emerges that photochemical addition of methanol to stilbene (**1**) is at least 30 times less efficient than *E,Z*-isomerization of (**1**). On the basis of the known[15] quantum yield ($\varphi = 0.5$) of the latter process, the upper limit for the quantum yield of MeOH addition to the alkenic bond of (**1**) is estimated to be 0.01. This value accounts for the fact that under the oxidative irradiation conditions (I_2/O_2) usually employed in previous studies, addition of MeOH to (**1**) has never been observed along with the rather efficient ($\varphi = 0.1$)[16] photoreaction of *Z*-(**1**) to phenanthrene (**5**).

Referring to *E,Z*-isomerization and formation of the corresponding phenanthrenes the addition of MeOH to 3,3′-dimethylstilbene (**6**) appears to be a relatively efficient photoprocess. Even under oxidative irradiation conditions, competition between methanol addition to (**6**) and conversion into the corresponding phenanthrenes was observed (Table 1).

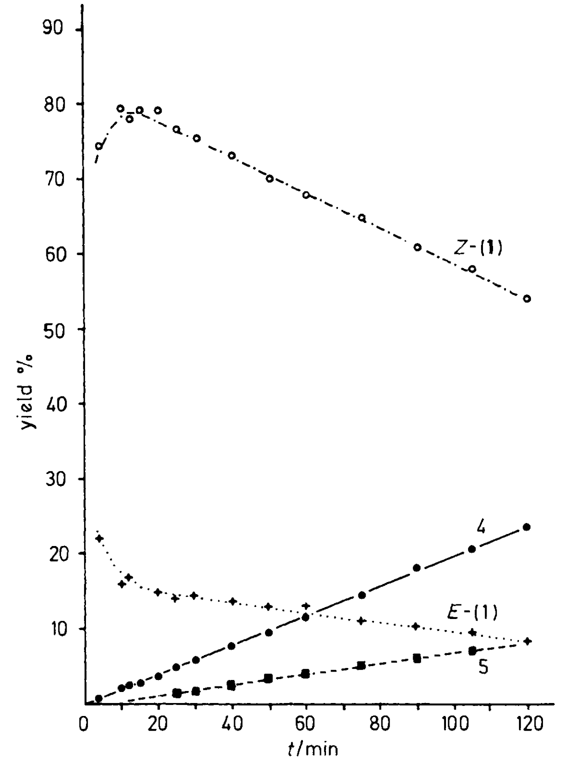


Figure 1. Irradiation (HPM) of stilbene *E*-(**1**) (4×10^{-4} mol dm^{-3}) in deaerated MeOH. Conversion of *E*-(**1**) and yields of *Z*-(**1**), 1-methoxy-1,2-diphenylethane (**4**) and phenanthrene (**5**) as a function of the irradiation time.

Reaction Mechanism.—To elucidate the mechanism of the photochemical methanol addition to stilbene (**1**) and its substituted derivatives, the following studies have been performed: (*a*) investigation of the influence of a strong acid on the rates of the photochemical methanol addition reaction. By way of this approach it should be possible to establish whether protonation of the excited state is involved in the formation of methanol adducts from stilbenes; (*b*) irradiations in MeOD at different wavelengths, in order to establish the isotope effect and stereochemistry of the photochemical methanol addition reaction and the effect of the wavelength thereupon.

Influence of acid on the rates of the photochemical methanol addition. Repeating the irradiation experiment outlined in Figure 1 with *trans*-stilbene [*E*-(**1**)] in the presence of a 20-fold excess (8×10^{-3} mol dm^{-3}) of H_2SO_4 resulted in a yield *vs.* time plot identical with that in Figure 1. This shows that for stilbene (**1**), neither the photochemical addition of methanol leading to (**4**), nor the photochemical *E,Z*-isomerization and cyclization reactions, leading to phenanthrene (**5**) are sensitive to acid catalysis.

Similar irradiation experiments performed with diphenylcyclopentene (**2**) reproduced essentially the results quoted for *E*-(**1**). On irradiation of (**2**) under the conditions stated in Figure 1, neither the rate of the photochemical methanol addition to (**2**), nor that of conversion into 9,10-cyclopentenophenanthrene were influenced by the presence of a 50-fold excess (0.02 mol dm^{-3}) of H_2SO_4.

It thus emerges that the photochemical addition of methanol to stilbene (**1**) and diphenylcyclopentene (**2**) does not involve protonation of the S_1 states of these compounds as a rate-determining step. In the case of stilbene (**1**), this conclusion is corroborated by the fact that the fluorescence of *trans*-stilbene *E*-(**1**) in methanol was not quenched observably by H_2SO_4, in concentrations up to 6.0 mol dm^{-3}.

Table 1. Irradiation (HPM, 120 min) of 3,3′-dimethylstilbene (**6**) (1.6×10^{-4} mol dm^{-3}) in air-saturated methanol. Influence of temperature and concentration of iodine ([I$_2$]) on the yield of the methanol adduct 1-methoxy-1,2-di(*m*-tolyl)ethane.

	yield of 1-methoxy-1,2-di(*m*-tolyl)ethane, (%)	
T/°C	$[I_2] = 0$	$[I_2] = 1.6 \times 10^{-4}$ mol dm^{-3}
−80	9.1	0
−60	15.4	1.4
22	18.4	3.6
40	26.0	—

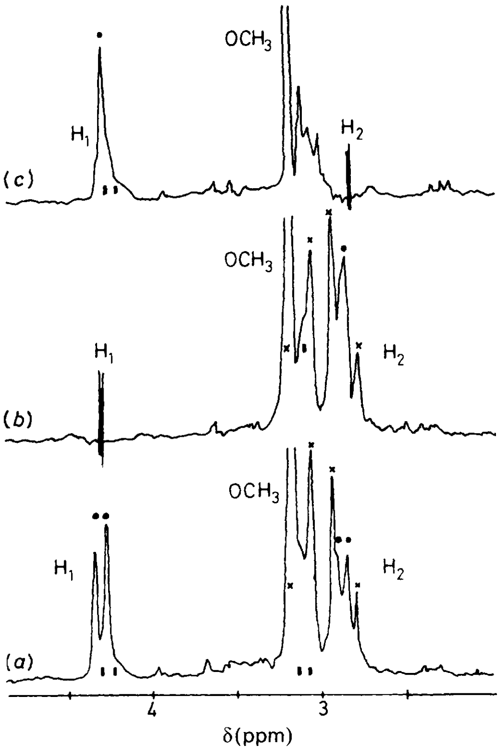


Figure 2. Aliphatic part of the 90 MHz ^{1}H n.m.r. spectrum of a mixture of [1-^{2}H]-(**4**) and 2-deuterio-1-methoxy-1,2-diphenylethane [*threo*- and *erythro*-2-^{2}H$_1$-(**4**)]. Normal spectrum (*a*) and spectra, spin-decoupled at H$_1$ (*b*) and at H$_2$ (*c*) of 2-^{2}H$_1$-**4**.

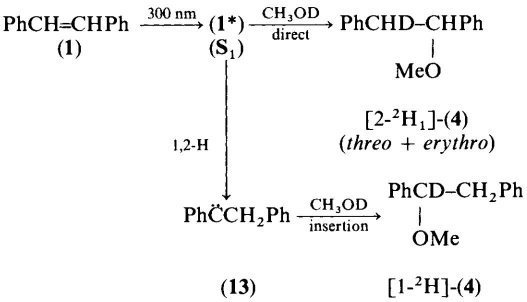
Irradiations in MeOD. In order to establish the stereochemistry of the photochemical methanol addition to stilbene (**1**), we irradiated *E*-(**1**) in MeOD at 300 nm. The n.m.r. spectrum (Figure 2) of the chromatographically separated MeOD adducts demonstrated unambiguously the presence of *threo*- and *erythro*-1-methoxy-2-deuterio-1,2-diphenylethane [2-^{2}H$_1$-(**4**) as well as the, previously unexpected 1-methoxy-1-deuterio-1,2-diphenylethane [1-^{2}H]-(**4**) (Scheme 3). From n.m.r. integration the ratio [1-^{2}H]-(**4**)/[2-^{2}H$_1$]-(**4**) was found to be 0.8 ± 0.1 (at 300 nm). These data are consistent with the c.i. mass spectrum which shows fragmentation peaks at *m*/*z* 122 {due to [1-^{2}H]-(**4**)} and at *m*/*z* 121 {due to [2-^{2}H$_1$]-(**4**)} in an intensity ratio of 0.85. From these results it follows, that addition of methanol to (**1**) involves the two competing pathways outlined in Scheme 3; *viz.* direct addition of methanol to the alkenic bond of excited (**1**) [(**1***)]† and insertion[17] of methanol by carbene (**13**), emerging from a 1,2-H shift in (**1***).

Table 2. Irradiation of stilbene *E*-(**1**), 4,4′-difluorostilbene (**7**) (Scheme 2, $R^1 = R^2 = F$) and 4-methoxystilbene (**8a**) (Scheme 2) in MeOD. Wavelength dependence of the rate ratio (r_{cat}/r_{dir}) of MeOD addition *via* the carbene (r_{car}) and direct (r_{dir}) pathway.

	r_{car}/r_{dir}		
λ/nm	(**1**)	(**7**)	(**8a**)
360	0.6 ± 0.1	0.8 ± 0.3	0
300	0.9 ± 0.3	1.3 ± 0.4	0
254	2.0 ± 0.5	2.1 ± 0.5	1.4 ± 0.5
185	>3	>3	—

Table 3. Irradiation of stilbene *E*-(**1**), 4,4′-difluorostilbene (**7**) (Scheme 2, $R^1 = R^2 = F$) and 4-methoxystilbene (**8a**) (Scheme 2) in MeOD. Wavelength dependence of the *threo*/*erythro* ratio (k_t/k_e) of MeOD adducts emerging *via* the direct pathway and of the photostationary state *Z*/*E* ratio of the parent stilbene.

	(**1**)		(**7**)		(**8a**)	
λ/nm	k_t/k_e	Z/E	k_t/k_e	Z/E	k_t/k_e	Z/E
360	0.7	18	0.04	15	0.5	0.9
300	0.8	5.7	0.04	3	0.4	8.2
254	1.8	1.9	0	1.4	0.1	1.2



Scheme 3.

The results presented in Table 2 indicate this conclusion to be valid for substituted stilbenes as well. As can be seen from Table 2, the ratio of the rates of methanol addition *via* the carbene (r_{car}) and direct (r_{dir}) route increases smoothly with decreasing irradiation wavelength λ.

The wavelength dependence of the *threo*-[2-^{2}H$_1$]-(**4**)/*erythro*-[2-^{2}H$_1$]-(**4**) ratio (k_t/k_e) was also investigated. The results have been collected in Table 3.

To evaluate the deuterium isotope effect on the yields of the direct photochemical methanol addition to stilbene (**1**) (Scheme 3), *E*-(**1**) was irradiated in a 1:1 (molar) mixture of MeOH and MeOD at 300 nm. From the observed yields of the methanol adducts (**4**), [1-^{2}H]-(**4**) and [2-^{2}H$_1$]-(**4**), the values of k_t/k_e (Table 3) and the isotope effect for insertion of carbene (**13**) (see below) into methanol, the isotope effect on the yield of [2-^{2}H$_1$]-(**4**) (*threo* + *erythro*, Scheme 3) was shown to be 2.8 ± 0.5. This value is much higher than for insertion of carbene (**13**) into methanol ($k_H/k_D = 1.4$, see below) and, considering the high polarity of methanol, points to a rather symmetrical transition state in the direct addition of methanol to the alkenic bond of (**1**).

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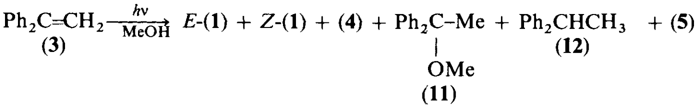
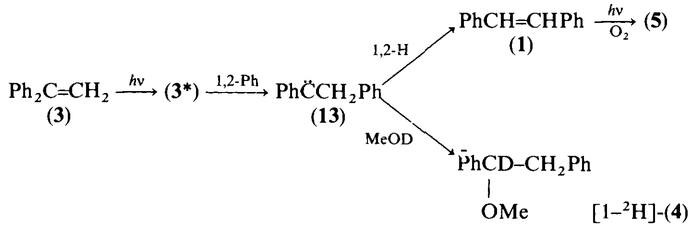
† On sensitized irradiation (300 nm, 24 h) in the presence of benzophenone (0.02 mol dm^{-3}), *E*-(**1**) (4.0×10^{-4} mol dm^{-3}) gave only *E*,*Z*-isomerization.

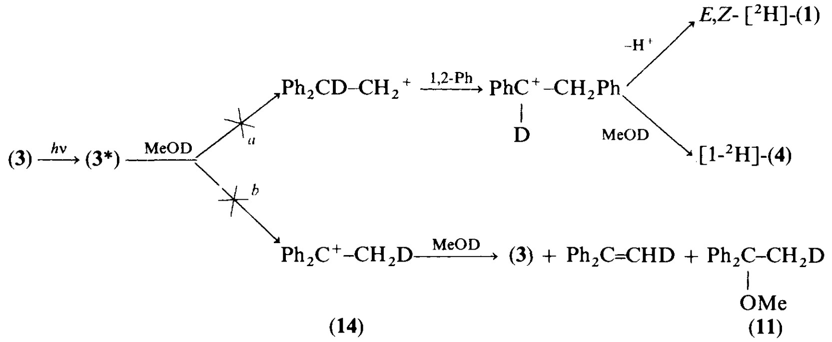


$$\underset{(3)}{Ph_2C{=}CH_2} \xrightarrow[MeOH]{h\nu} E\text{-}(1) + Z\text{-}(1) + (4) + \underset{\underset{(11)}{OMe}}{Ph_2C{-}Me} + \underset{(12)}{Ph_2CHCH_3} + (5)$$

Scheme 4.



Scheme 5.



Scheme 6.

The isotope effect for insertion of carbene (**13**) in methanol was evaluated by generating this carbene independently, from 1,1-diphenylethene (**3**). On direct irradiation in deaerated MeOH at 254 nm, this compound was observed to undergo Markovnikov addition of MeOH to the alkenic bond, affording 1-methoxy-1,1-diphenylethane (**11**) (Scheme 4), as well as rearrangement, leading to 1-methoxy-1,2-diphenylethane (**4**), phenanthrene (**5**) and traces of stilbene *E*- and *Z*-(**1**). Along with these photoreactions, photoreduction to 1,1-diphenylethane (**12**), and extensive photopolymerization also take place.

Analogous to the case of stilbene (Figure 1), the progress of this photoreaction of (**3**) in methanol was monitored as a function of the irradiation time. The resulting yield *vs.* time curves are given in Figure 3. The yield *vs.* time curves of *E*- and *Z*-(**1**) could not be evaluated, due to the very low abundances [$<0.5\%$, based on reacted (**3**)] of these compound among the photoproducts of (**3**).

According to Figure 3, the methoxydiphenylethanes (**4**) and (**11**) and 1,1-diphenylethane (**12**) are primary photoproducts of (**3**). On the other hand, phenanthrene (**5**), being observable only on prolonged (>1 h) irradiation of (**3**), clearly emerges as a secondary photoproduct of (**3**) in this experiment. This result proves that (**4**) is not formed from (**3**) *via* photochemical methanol addition to *E*- or *Z*-(**1**) (Scheme 2).

Considering the formation of the rearrangement products stilbene [*E*- and *Z*-(**1**)], methanol adduct (**4**) and phenanthrene (**5**) from 1,1-diphenylethene, rationalizing these rearrangement products must involve a carbene intermediate (**13**) (Scheme 5). A radical reaction would involve the relatively stable $\cdot CH_2OH$ rather than the $CH_3O\cdot$ radical.[18] Because methanol adducts derived from the former radical have not been observed, a radical mechanism appears unlikely. The possibility of an ionic mechanism, involving protonation of excited (**3**) [(**3***), Scheme 6, pathway *a*] was rejected on the basis of carbenium ion stabilities. Conclusive evidence regarding the intermediacy of carbene (**13**) was obtained from the results of irradiation of (**3**)

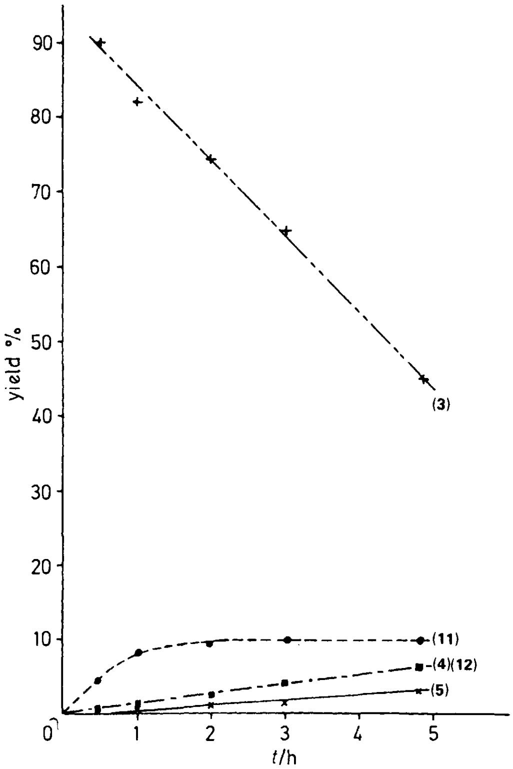
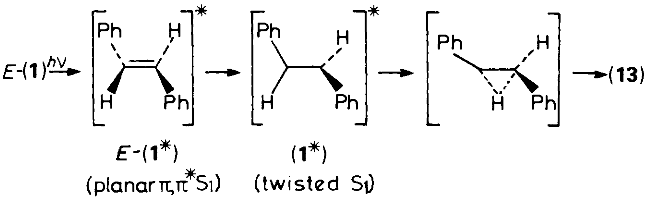


Figure 3. Irradiation (254 nm) of 1,1-diphenylethene (**3**) (10^{-3} mol dm^{-3}) in deaerated MeOH. Conversion of (**3**) and yields of 1-methoxy-1,2-diphenylethane (**4**), phenanthrene (**5**), 1-methoxy-1,1-diphenylethane (**11**) and 1,1-diphenylethane (**12**) as a function of the irradiation time. The yield *vs.* time curves of *E*- and *Z*-(**1**) could not be evaluated due to the low abundances ($<0.5\%$) of these compounds among the photoproducts of (**3**).

in MeOD. As expected for its formation *via* insertion by carbene (**13**) in methanol, (**4**) (Schemes 5 and 6) was obtained exclusively with D and OCH_3 substituents at the same carbon atom [1-^{2}H]-(**4**). The fact that in this experiment no D incorporation was observed in *E*- and *Z*-(**1**), (**5**), and unchanged (**3**), excludes the ionic pathway *b* depicted in Scheme 6 from being involved in the formation of stilbene [*E*- and *Z*-(**1**)] and methanol adduct (**4**) from (**3**). In a subsequent experiment, 1,1-diphenylethene (**3**) was irradiated in a 1 : 1 (molar) mixture of MeOH and MeOD. After chromatographic separation of the methanol adducts, the isotope effect (k_H/k_D) on the yield of (**4**) was found to be 1.4 ± 0.2, both by n.m.r. and mass spectroscopy. This value is in excellent agreement with that obtained for a genuine insertion of a singlet carbene into the O–H(D) bond of MeOH(D).[17]

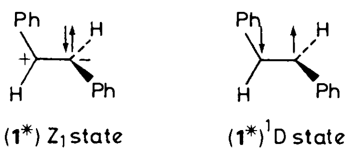
Nature of the excited state. The nature of the excited state involved in the photochemical addition of methanol to stilbene (**1**) and the rearrangement of this compound to carbene (**13**) is the final subject to be considered. As mentioned in the introduction, rearrangement to carbene (**13**) can occur from a Rydberg π,R(3s) or a π,π* excited state of (**1**). At irradiation wavelengths ≥254 nm † (Table 2) the former possibility can be rejected, since the photon energies (3.4–4.9 eV) involved are well below the $\pi \rightarrow R(3s)$ transition energies reported[19] for alkenes. Because of the absence of radical reaction products from the T_1 state and the failure of stilbene (**1**) to undergo methanol addition on sensitized irradiation,[17] the reactive excited state (**1***) (Scheme 3) was concluded to be the lowest excited S_1 state. The ability of excited stilbene (**1***) in methanol to rearrange into carbene (**13**), obviously implies that the parent S_1 state is highly (*ca.* 90°) twisted around the alkenic bond; in order to provide the geometry required ‡ for the 1,2-H shift involved (Scheme 7).



Scheme 7.

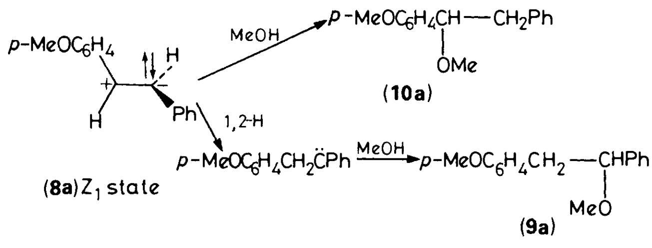
Presumably, a similar consideration applies to the rearrangement (Scheme 4) of excited diphenylethene (**3***) to carbene (**13**).

The rearrangement of excited stilbene (**1***) to carbene (**13**) might involve either a zwitterionic (Z_1) or a non-polar (^{1}D) twisted excited S_1 state.[20] MO-CI calculations on propene[21] predict the rearrangement $Z_1 \longrightarrow$ (**13**) to be allowed, hydrogen migrating from the negatively to the positively charged carbon atom. Though these calculations predict the transition $^1D \rightarrow$ (**13**) to be symmetry-forbidden, it still might occur from a vibrationally unrelaxed ^{1}D state.



Scheme 8.

The available experimental evidence appears inconsistent with the former alternative. If, in the case of 4-methoxystilbene (**8a**) (Scheme 2) the direct and the carbene pathway for addition of methanol are assumed to involve a common Z_1 state, both regioisomeric methoxy(4-methoxy)bibenzyls (**9a**) and (**10a**) would be expected (Scheme 9). The fact that on irradiation at 254 nm, where both these pathways are operative (Table 2) exclusively β-methoxy(4-methoxy)bibenzyl (**10a**) was observed, is not consistent with this theory. Of course, a highly polar Z_1 state should be liable to protonation reactions, particularly by strong acids such as H_2SO_4. This assumption appears in contradiction with the observation that sulphuric acid does not affect the rate of the photochemical methanol addition reaction to stilbene (**1**) or 1,2-diphenylcyclopentene (**2**). It is also inconsistent with the failure of H_2SO_4 to quench the fluorescence of *E*-(**1**) in MeOH and with the complete lack of D incorporation (g.c.–m.s.) in phenanthrene (**5**) and stilbene (**1**) recovered from irradiations of *E*-(**1**) in MeOD. Since the presence of electron-donating substituents obviously stabilizes the Z_1 state relative to the non-polar ^{1}D excited state and the ground state, enhanced partition of the carbene pathway in the photochemical addition of methanol to stilbenes containing such substituents should be expected. Inspection of Table 2 however reveals exactly the opposite trend; the highest r_{car}/r_{dir}-values being observed in 4,4′-difluorostilbene (**7**) (Scheme 2, $R^1 = R^2 = F$).



Scheme 9.

The alternative of a non-polar ^{1}D state as the precursor for the stilbene–carbene rearrangement [$(\mathbf{1^*}) \longrightarrow (\mathbf{13})$; Scheme 7], provides a more satisfactory account for the experimental data discussed in the previous paragraph. Within this assumption the wavelength dependence of r_{car}/r_{dir} (Table 2) merely reflects the creation of vibrationally unrelaxed ^{1}D states on excitation of stilbenes with highly energetic photons. According to the widths of the u.v. absorption bands [*E*-(**1**): $\Delta\nu_{\frac{1}{2}} = 6\,000$ cm^{-1}; *E*-(**8**): $\Delta\nu_{\frac{1}{2}} = 9\,000$ cm^{-1}] excited (**8**) should exhibit a higher rate of internal conversion (through vibrational relaxation) than (**1**). This provides an adequate explanation for the observed substituent effect on r_{car}/r_{dir} (Table 2).

In the case of direct addition of methanol to the alkenic bond of stilbene (**1**), the geometry of the excited S_1 state involved is less obvious. According to Scheme 3, direct addition of methanol to excited stilbene (**1***) affords both possible diastereoisomers *threo*- and *erythro*-[2-$^2H_1$]-(**4**). As outlined in Scheme 10, a twisted S_1 state of stilbene *E*- or *Z*-(**1**) might be considered as a common precursor of these photoproducts: Attack of both enantiomers of this *chiral* S_1 state by MeOD would explain the occurrence of *threo*- and *erythro*-[2-$^2H_1$]-(**4**). In the case of a vibrationally relaxed twisted S_1 state, a wavelength-independent ratio of these diastereoisomers should be expected. By this assumption alone the experimental data given in Table 3 cannot be accounted for.

On the other hand, it was observed that the necessarily planar diphenylcyclopentene (**2**) undergoes photochemical addition of

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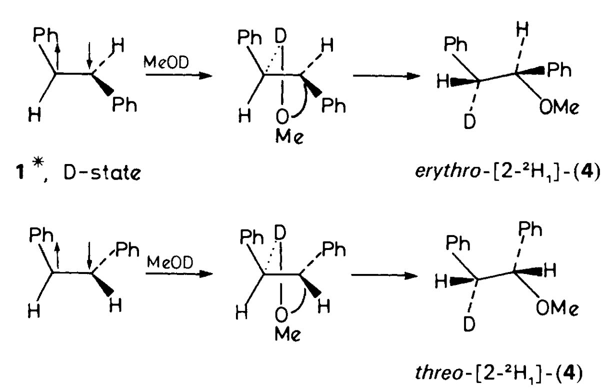
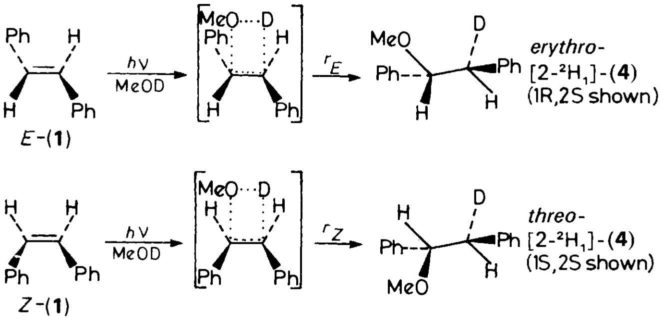
† At 185 nm, a Rydberg π,R(3s) state of stilbene is likely to be the precursor of carbene (**13**) (references 5, 7, 22 and 23). Unfortunately, the difficulties in obtaining reproducible r_{car}/r_{dir} ratios (Table 2) at this wavelength, prevented further investigation of this possibility.

‡ According to MO-CI calculations on ethene (reference 23) the possibility of an in-plane 1,2-H shift from planar *E*- or *Z*-(**1**) need only be considered at very high excitation energy where *E*,*Z*-(**1**) might be excited into a π,R(3s) Rydberg state.



Scheme 10.

MeOH at roughly the same rate as stilbene (**1**). This suggests the possibility of direct addition of methanol by attack of MeOD on a planar $^1(\pi,\pi^*)$ state of (**1**). Due to efficient photochemical *E,Z*-isomerization, both *E*- and *Z*-(**1**) are present (Figure 1) in the photostationary state resulting from irradiation of *E*-(**1**). Hence, *threo*- and *erythro*-[2-$^2H_1$]-(**4**) can alternatively be rationalized as the products of *cisoid* addition of MeOD to the planar, unrelaxed $^1(\pi,\pi^*)$ states of *E*- and *Z*-(**1**) (Scheme 11), respectively.



Scheme 11.

Our present knowledge is insufficient to establish the extent to which twisted and planar S_1 states are involved in the direct (Scheme 3) photochemical addition of methanol to stilbenes. The available experimental evidence suggests k_t/k_e to be determined by the competition of a planar, unrelaxed $^1(\pi,\pi^*)$ state and a twisted ^{1}D state for direct addition (Scheme 3) of methanol to the alkenic bond of stilbenes.

Conclusions

Photochemical addition of methanol to the alkenic bond of stilbene (**1**) is possible under strictly anaerobic conditions. The scope of this reaction appears to be fairly general, including stilbene derivatives substituted with electron-withdrawing as well as electron-donating groups at the aromatic rings. In the case of substituted stilbenes, Markovnikov addition of methanol is preferred.

The photochemical addition of methanol to stilbene (**1**) and its substituted derivatives involves two distinct, competitive pathways, *i.e.* (*i*) Rearrangement *via* a 1,2-hydrogen shift, affording an intermediate carbene (**13**), which is inserted into the O–H bond of methanol and (*ii*) direct addition of methanol to the alkenic bond.

Both these pathways were shown to be operative in a very similar photochemical methanol-addition reaction to 1,1-diphenylethene (**3**). In this case, carbene intermediate (**13**) arises *via* a 1,2-phenyl shift.

The insertion of carbene (**13**) into the O–H bond of methanol represents the second example of intermolecular trapping of a carbene intermediate in the photoisomerization of an alkene. The only other case, in which intermolecular insertion has been shown to compete appreciably with intramolecular insertion into the neighbouring β-C–H bond, concerns the carbene intermediate formed on irradiation of tri-t-butylethylene.[5,8] However, unlike (**13**) the latter carbene is subject to exceptional steric congestion, due to the presence of three t-butyl substituents. The present work demonstrates, that extreme steric congestion is not a prerequisite for competition between intra- and inter-molecular insertion of carbene intermediates, formed in the photoisomerization of an alkene.

In the case of stilbenes, the wavelength and substituent dependence of the rates of these competing pathways and the observation that both pathways give the same MeOH adduct, lead to the conclusion that the carbene pathway presumably involves a vibrationally unrelaxed twisted excited singlet (^{1}D) state.

The pathway of direct addition of methanol to the alkenic bond of stilbenes may involve either a twisted (^{1}D) or a planar (π,π^*) excited singlet state. The actual intermediacy of a twisted ^{1}D excited state emerges from its ability to rearrange to carbene (**13**). The possibility of concerted addition of methanol to a planar (π,π^*) state of stilbenes emerges from the ability of the obligatory planar 1,2-diphenylcyclopentene (**2**) to undergo photochemical addition of methanol at roughly the same rate as stilbene (**1**) itself.

Experimental evidence, excluding the involvement of highly polar, zwitterionic excited states in both the carbene and the direct pathway of photochemical methanol addition to stilbene has been presented.

Experimental

Starting Materials.—(*E*)-Stilbene *E*-(**1**) and 1,1-diphenylethene (**3**) were obtained commercially. 1,2-Diphenylcyclopentene (**2**),[22] 3,3′-dimethylstilbene (**6**), 4,4′-difluorostilbene (**7**), 4-methoxystilbene (**8a**), 4-methoxy-4′-methylstilbene (**8b**), and 4-methylstilbene (**8c**) were synthesized according to known[22,23] procedures. All starting materials were purified by recrystallization, sublimation, distillation, or column chromatography prior to use.

Irradiations.—Preparative irradiations were performed in N_2-deaerated methanol (u.v.: transmittance >95% at 254 nm), employing the following light sources: Philips UV-A TL (360 and 300 nm), Philips TUV G15T8 (254 nm) and Osram HNS 10 (185 nm; Suprasil irradiation vessel). For the evaluation of yield *vs.* time plots (Figures 1 and 3), irradiations were carried out either with 50 cm³ samples, in a Rayonet RPR-100 photochemical reactor equipped with a merry-go-round or in an N_2-purged 200 cm³ irradiation vessel equipped with a liquid-nitrogen-cooled (MeOH, $-90 < T < 25$ °C) quartz finger and a sampling facility. In the latter case, 0.2 cm³ aliquots were taken at 2 min intervals and subsequently analysed by g.l.c. Samples originating from irradiations in the presence of H_2SO_4 were neutralized with OH^--exchanged Dowex IRA-400 ion-exchange resin prior to injection.

General Methods.—Isolation of the photoproducts was achieved by t.l.c. and column chromatography on silica gel (Merck 60, 70–230 mesh) employing CCl_4 or hexane–benzene (6:1) as the eluant. Solid components [*e.g.* (**10a**)] obtained in this way were recrystallized from MeOH. Compositions of photoproduct mixtures were determined by g.l.c., employing a HP 5790 gas chromatograph equipped with HP or Chrompack capillary columns, a HP 3390 recording integrator and a flame ionization detector. The response of the detector was assumed to be proportional to the number of carbon atoms present in the component detected. Characterization of the photoproducts involved ^{1}H n.m.r. [Bruker WH-90 (90 MHz) and WM-500 (500 MHz) spectrometers, internal reference: $SiMe_4$], mass spectroscopy (VG 70-70 MS equipped with a g.l.c. facility similar to that quoted above) and chemical synthesis of authentic samples. In several cases, values of δ, $\Delta\delta$, and J were obtained from a least-squares fit of these quantities into the experimental (AB-, ABX- or AB_2-type n.m.r. spectrum.

1-*Methoxy*-1,2-*diphenylethane* (**4**). Authentic (**4**) was prepared from 1,2-diphenylethanol in 70% yield;[13] δ(90 MHz; $CDCl_3$) 2.76–3.23 [2 H, m (AB of ABX), $J_{2,2'}$ 13.68 Hz, 2-H and 2-H′], 2.88 ($J_{1,2}$ 5.98 Hz, 2-H), 3.11 ($J_{1,2'}$ 7.26 Hz, 2-H′), 3.18 (3 H, s, OCH_3), 4.32 (1 H, t, 1-H), and 7.08–7.34 (10 H, m, ArH); *m/z* (c.i., CH_4) 209 [11%, $M^+ + 29(C_2H_5{}^+) - 32$(MeOH)], 182 (16), 181 [$M^+ + 1(H^+) - 32$(MeOH), 100], 135 [23, $M^+ + 1(H^+) - 78(C_6H_6)$], 121 (71, $PhCHOMe^+$), 105 (11), and 91 (12).

1-*Deuterio*-1-*methoxy*-1,2-*diphenylethane* [1-^{2}H]-(**4**). This compound was obtained *via* rearrangement of (**3**). δ(500 MHz; $CDCl_3$) 2.877 (1 H, d, $J_{2,2'}$ 13.82 Hz, 2-H), 3.108 (1 H, d, 2-H′), 3.183 (3 H, s, OCH_3), 7.08–7.33 (10 H, m, Ar H); *m/z* (c.i., CH_4) 210 (11%), 183 (15), 182 [100, $M^+ + 1(H^+) - 32$(MeOH)], 136 [22, $M^+ + 1(H^+) - 78(C_6H_6)$], 122 (57, $PhCDOMe^+$).

2-*Deuterio*-1-*methoxy*-1,2-*diphenylethane* [2-^{2}H]-(**4**). *erythro*-[2-$^2H_1$]-(**4**). δ(500 MHz; $CDCl_3$) 2.866 (1 H, br d, $J_{1,2}$ 6.0 Hz, 2-H), 3.183 (3 H, s, OCH_3), 4.315 (1 H, br d, H_1), and 7.08–7.33 (10 H, m, Ar H). *threo*-[2-^{2}H]-(**4**) δ(500 MHz; $CDCl_3$) 3.095 (1 H, br d, $J_{1,2}$ 7.2 Hz, 2-H) and 3.183 (3 H, s, OCH_3), 4.315 (1 H, br d, 1-H), 7.08–7.33 (10 H, m, Ar H); *m/z* {(c.i., CH_4, mixture of *erythro*- and *threo*-[2-$^2H_1$]-(**4**)} 210 (12%), 183 (16), 182 [100, $M^+ + 1(H^+) - 32$(MeOH)], 136 (13), 121 (65), 106 (7).

1-*Methoxy*-1,2-*diphenylcyclopentane* [MeOH *Adduct of Diphenylcyclopentene* (**2**)]. δ(90 MHz; $CDCl_3$) 1.77–2.46 (6 H, m, 3-, 4- and 5-H), 3.05 (3 H, s, OCH_3), 3.1–3.5 (1 H, m, 2-H), and 6.69–7.13 (10 H, m, Ar H); *m/z* (c.i., CH_4) 253 [5%, $M^+ + 1(H^+)$], 252 (10, M^+), 250 (6), 222 (19), 221 [100, $M^+ + 1(H^+) - 32$(MeOH)], 220 (14), 175 (30), 147 (18), 145 (18), 143 (30), 117 (72), and 91 (13).

1-*Methoxy*-1,2-*di*(m-*tolyl*)*ethane* [MeOH *adduct of* (**6**), *Table* 1]. δ(90 MHz; $CDCl_3$) 2.31 [3 H, s, 1-(*m*-$CH_3C_6H_4$)], 2.35 [3 H, s, 2-(*m*-$CH_3C_6H_4$)], 2.70–3.17 [2 H, m (AB of ABX), $J_{2,2'}$ 13.73 Hz, 2-H, 2-H′], 2.83 ($J_{1,2}$ 5.26 Hz, 2-H), 3.03 ($J_{1,2'}$ 7.90 Hz, 2-H′) 3.17 (3 H, s, OCH_3), 4.27 [1 H, q (X of ABX), 1-H], and 6.87–7.29 (8 H, m, Ar H); *m/z* (c.i. CH_4) 237 (12%), 210 (17), 209 [100, $M^+ + 1(H^+) - 32$(MeOH)], 149 (13), 136 (5), 135 (47), 119 (4), 105 (4).

1-*Deuterio*-1,2-*di*(p-*fluorophenyl*)-1-*methoxyethane* [MeOD *adduct of* (**7**) (*Scheme* 2, $R^1 = R^2 =$ F), via *carbene pathway*, *Table* 2]. δ(90 MHz; $CDCl_3$) 2.71–3.15 [2 H, q (AB), $J_{2,2'}$ 13.6 Hz, 2-H, 2-H′], 3.17 (3 H, s, OCH_3), and 6.74–7.31 (8 H, m, Ar H).

2-*Deuterio*-1,2-*di*(p-*fluorophenyl*)-1-*methoxyethane* [MeOD *adduct of* (**7**), via *direct pathway*, *Table* 3]. *erythro*-isomer: δ(90 MHz; $CDCl_3$) 2.79 (1 H, br d, $J_{1,2}$ 6.2 Hz, 2-H), 3.17 (3 H, s, OCH_3), 4.24 (1 H, br d, 1-H), 6.74–7.31 (8 H, m, Ar H). *threo*-isomer: δ 3.00 (1 H, br d, $J_{1,2}$ 7 Hz, 2-H), 3.17 (3 H, s, OCH_3), 4.21 (1 H, br d, 1-H), 6.74–7.31 (8 H, m, Ar H).

1-*Methoxy*-2-(p-*methoxyphenyl*)-1-*phenylethane* [(**9a**), *hypothetical anti-Markovnikov* MeOH *adduct of* (**8a**)]. The Grignard reaction[23] of *p*-methoxybenzylmagnesium bromide and benzaldehyde afforded 2-(*p*-methoxyphenyl)-1-phenylethanol, which was converted into the lithium salt by treatment of the THF solution with a stoicheiometric quantity of BuLi at 0 °C. Following the addition of an excess of MeI, the solution was refluxed for 3 h. Evaporation of the solvent afforded a yellow residue, which was boiled with CCl_4 and filtered. The resulting filtrate was concentrated to *ca.* 2 cm^3 and subsequently purified by column chromatography, to afford (**9a**) [Purity (g.l.c., n.m.r.) 95%] as a colourless oil in 60% overall yield. (Found: C, 78.75; H, 7.55. Calc. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%); δ(90 MHz; $CDCl_3$) 2.68–3.18 [2 H, m (AB of ABX), $J_{2,2'}$ 13.9 Hz, 2-H, 2-H′], 2.82 ($J_{1,2}$ 6.12 Hz, 2-H), 3.04 ($J_{1,2'}$ 7.38 Hz, 2-H′), 3.18 (3 H, s, 1-OCH_3), 3.72 (3 H, s, *p*-$CH_3OC_6H_4$), 4.26 [1 H, t (X of ABX), 1-H], 6.70–7.05 [4 H, q (AB), $J_{ortho,meta}$ 8.46 Hz, *p*-$CH_3OC_6H_4$], and 7.14–7.39 (5 H, m, C_6H_5); *m/z* (c.i., CH_4) 243 [7%, $M^+ + 1(H^+)$], 242 (28, M^+), 212 (7), 211 (45), 165 (10), 122 (68, $MeOC_6H_4Me^{+\bullet}$), 121 (100, $MeOC_6H_4CH_2{}^+$), 107 (7), 106 (12), 105 (19), 91 (44), 78 (28), and 77 (63).

1-*Methoxy*-1-*phenyl*-2-(p-*tolyl*)*ethane* (**9c**). δ(90 MHz; $CDCl_3$) 2.30 (3 H, s, $CH_3C_6H_4$), 2.72–3.22 [2 H, m (AB of ABX), $J_{2,2'}$ 13.8 Hz, 2-H, 2-H′] 2.85 ($J_{1,2}$ 5.87 Hz, 2-H), 3.07 ($J_{1,2'}$ 7.36 Hz, 2-H′), 3.18 (3 H, s, OCH_3), 4.29 [1 H, t (X of ABX), 1-H], and 7.0–7.4 (9 H, m, Ar H).

1-*Methoxy*-1-(p-*methoxyphenyl*)-2-*phenylethane* (**10a**). This compound was prepared from *p*-methoxybenzaldehyde and benzylmagnesium bromide according to the procedure outlined for (**9a**). Contrary to the latter, crude (**10a**) was isolated as a solid which was readily purified by crystallization from MeOH (10 cm^3 g^{-1}) to give colourless crystals (yield 70%) m.p. 51–52 °C and 99.5% (g.l.c.) purity (Found: C, 79.25; H, 7.55. Calc. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%); δ(90 MHz; $CDCl_3$) 2.73–3.24 [2 H, m, (AB of ABX), $J_{2,2'}$ 13.61 Hz, 2-H, 2-H′], 2.86 ($J_{1,2}$ 6.19 Hz, 2-H), 3.11 ($J_{1,2'}$ 7.31 Hz, 2-H′), 3.15 (3 H, s, 1-OCH_3), 3.78 (3 H, s, *p*-$CH_3OC_6H_4$), 4.26 [1 H, t (X of ABX), 1-H], 6.78–7.18 [4 H, q (AB), $J_{ortho,meta}$ 8.50 Hz, *p*-$CH_3OC_6H_4$], and 6.99–7.28 (5 H, m, C_6H_5); *m/z* (c.i., CH_4) 243 [7%, $M^+ + 1(H^+)$], 242 (30, M^+), 212 (5), 211 (26), 165 (6), 153 (7), 152 (59, $MeOC_6H_4CH_2OMe^{+\bullet}$), 151 (100, $MeOC_6H_4CHOMe^+$), 136 (29), 135 (60), 121 (9), 108 (14, $MeOC_6H_5{}^{+\bullet}$), 92 (12), 91 (40), 78 (9), and 77 (16).

1-*Deuterio*-1-*methoxy*-1-(p-*methoxyphenyl*)-2-*phenylethane* {[1-^{2}H]-(**10a**), MeOD *adduct of* (**8a**), via *carbene pathway*, *Table* 2}. δ(90 MHz; $CDCl_3$) 2.74–3.18 [2 H, m (AB), $J_{2,2'}$ 13.5 Hz, 2-H, 2-H′], 2.84 (H_2), 3.08 ($H_{2'}$), 3.15 (3 H, s, 1-OCH_3), 3.78 (3 H, s, *p*-$CH_3OC_6H_4$), 6.77–7.16 [4 H, q, (AB), $J_{ortho,meta}$ 8.5 Hz, *p*-$CH_3OC_6H_4$], and 7.00–7.30 (5 H, m, C_6H_5).

2-*Deuterio*-1-*methoxy*-1-(p-*methoxyphenyl*)-2-*phenylethane* {[2-$^2H_1$]-(**10a**), MeOD *adduct of* (**8a**), via *direct pathway*, *Table* 3}, *erythro*-isomer: δ(90 MHz; $CDCl_3$) 2.84 (2 H, br d, $J_{1,2}$ 6.3 Hz, 2-H), 3.15 (3 H, s, 1-OCH_3), 3.79 (3 H, s, *p*-$CH_3OC_6H_4$), 4.26 (1 H, br d, 1-H), 6.77–7.16 (4 H, AB, $J_{ortho,meta}$ 8.5 Hz, *p*-$CH_3OC_6H_4$], and 7.00–7.30 (5 H, m, C_6H_5); *threo*-isomer: δ 3.08 (2 H, br d, $J_{1,2}$ 7 Hz, 2-H), 3.15 (3 H, s, 1-OCH_3), 3.79 (3 H, s, *p*-$CH_3OC_6H_4$), 4.25 (1 H, br d, H_1), 6.77–7.16 (4 H, q, AB, $J_{ortho,meta}$ 8.5 Hz, *p*-$CH_3OC_6H_4$], and 7.00–7.30 (5 H, m, C_6H_5).

1-*Methoxy*-1-(p-*methoxyphenyl*)-2-(p-*tolyl*)*ethane* (**10b**). δ(90 MHz; $CDCl_3$) 2.29 (3 H, s, $CH_3C_6H_4$) 2.70–3.21 [2 H, m (AB of ABX), $J_{2,2'}$ 13.8 Hz, 2-H, 2-H′], 2.83 ($J_{1,2}$ 6.3 Hz, 2-H), 3.07 ($J_{1,2'}$ 7.2 Hz, 2-H′), 3.16 (3 H, s, 1-OCH_3), 3.80 (3 H, s, *p*-$CH_3OC_6H_4$), 4.25 [1 H, t (X of ABX), 1-H], 6.80–7.20 [4 H, q (AB), $J_{ortho,meta}$ 8.47 Hz, *p*-$CH_3OC_6H_4$], and 7.01 (4 H, s, *p*-$CH_3C_6H_4$, *ortho*- and *meta*-H′s coincidentally having identical δ-values); *m/z* (c.i., CH_4) 253 (11%), 226 (17), 225 [100, $M^+ + 1(H^+) - 32$(MeOH)], 165 (6), 151 (34, $MeOC_6H_4CHOMe^+$), 149 (29), and 135 (12).

1-*Methoxy*-2-*phenyl*-1-(p-*tolyl*)*ethane* (**10c**). δ(90 MHz; $CDCl_3$) 2.34 (3 H, s, $CH_3C_6H_4$), 2.74–3.24 [2 H, m (AB of ABX), $J_{2,2'}$ 13.7 Hz, 2-H, 2-H′], 2.88 ($J_{1,2}$ 5.96 Hz, 2-H), 3.10 ($J_{1,2'}$ 7.34 Hz, 2-H′), 3.17 (3 H, s, OCH_3), 4.29 [2 H, t (X of ABX), 1-H], and 7.0–7.4 (9 H, m, Ar H); *m/z* (c.i., CH_4) 195 [7%, $M^+ + 1(H^+) - 32$(MeOH)], 136 (11), 135 (100), 121 (25), 119 (7), 105 (6), 91 (22), and 77 (7).

1-*Methoxy*-1,1-*diphenylethane* (**11**). This compound was synthesized according to the literature.[13] δ(90 MHz; $CDCl_3$)

1.86 (3 H, s, CH_3), 3.16 (3 H, s, OCH_3), and 7.13–7.43 (10 H, m, Ar H); *m/z* (c.i., CH_4) 209 (8%), 198 (6), 197 [38, $M^+ + 1(H^+) - 16(CH_4)$], 182 (13), 181 [82, $M^+ + 1(H^+) - 32(MeOH)$], 136 (10), and 135 (100).

2-*Deuterio*-1-*methoxy*-1,1-*diphenylethane* [2-$^2H_1$]-(**11**). δ(90 MHz; $CDCl_3$) 1.85 (2 H, br s, CH_2D), 3.16 (3 H, s, OCH_3), and 7.1–7.4 (10 H, m, Ar H); *m/z* (c.i., CH_4) 210 (8%), 197 [28, $M^+ + 1(H^+) - 17(CH_3D)$], 183 (17), 182 (76), 137 (11), and 136 (100).

2-*Methoxy*-1,1-*diphenylethane* [*hypothetical anti-Markovnikov* MeOH *adduct of* (**3**)]. δ(90 MHz; $CDCl_3$)[13] 3.37 (3 H, s, OCH_3), and 3.87–4.37 [3 H, m (AB_2), $J_{1,2}$ 7.32 Hz, 1-, 2-H], 7.25 (10 H, br s, Ar H); *m/z* (c.i., CH_4) 209 (11%), 182 (16), 181 [100, $M^+ + 1(H^+) - 32(MeOH)$], 167 (57), 165 (7), and 135 (15).

1,1-*Diphenylethane* (**12**). Authentic (**12**) was obtained by catalytic hydrogenation of (**3**). δ(90 MHz; $CDCl_3$)[24] 1.64 (3 H, d, $J_{1,2}$ 7.32 Hz, 2-H), 4.15 (1 H, q, 1-H), and 7.23 (10 H, s, Ar H); *m/z* (c.i., CH_4) 211 (8%), 184 (14), 183 (M^+, 100), 105 (42); *m/z* (70 eV)[25] 183 (3%), 182 (18, M^+), 168 (5), 167 (36), 165 (5), 106 (10), and 105 (100).

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