Photochemistry of Arylbutadienes. Part 3.[1,2] Mechanisms of Photo-addition of Methanol to 1-Arylbutadienes

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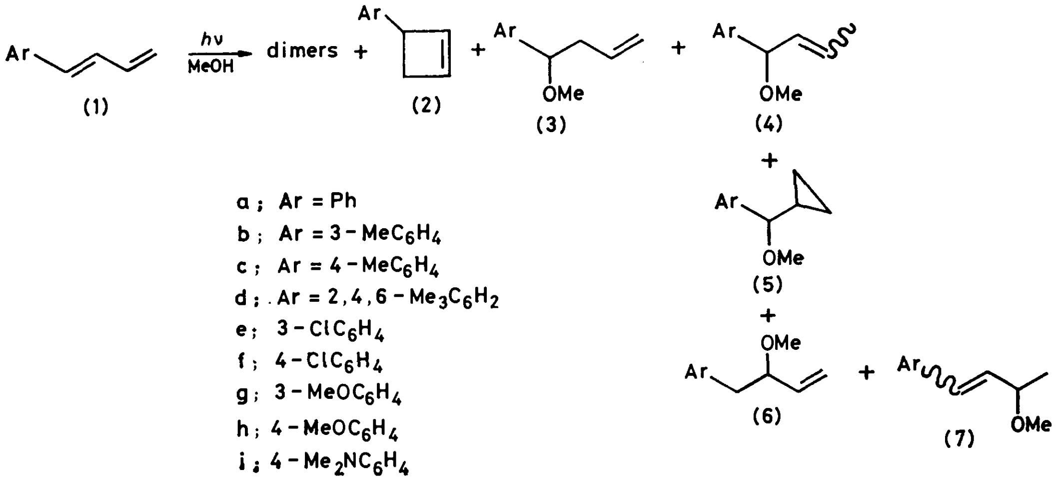
The mechanism of formation of methyl ethers from irradiation of 1-arylbutadienes in methanol has been studied by deuterium labelling, fluorescence quenching, sensitisation, and kinetic studies. Cyclopropylmethyl ethers arise by a bicyclobutane mechanism; allyl and homoallyl ethers are formed by reaction of methanol with the ${}^1B_u$-like excited singlet diene to produce carbocation intermediates.

IRRADIATION of aliphatic and alicyclic dienes in hydroxylic solvents has been studied extensively;[3] the photoaddition products are homoallyl, cyclobutyl, cyclopropylmethyl, and allyl ethers, alcohols, or esters. The first three types of product have been shown to arise from thermal addition of solvent to a photochemically-produced bicyclobutane,[4-6] but the mechanism of formation of the allyl products is not known. A triplet mechanism has been suggested[5,7] because two examples of sensitisation are known, and Dauben has suggested that the vibrationally excited ground-state diene is involved,[5] but other interpretations of these sensitisation results seem probable.



SCHEME 1

We recently reported that the photoaddition of methanol to phenyl-substituted butadienes gives similar products to those of aliphatic dienes;[1] in particular, Scheme 1 shows the products from 1-arylbutadienes, for which studies of substituent effects suggest a carbocation intermediate.[2] We now report further mechanistic evidence, and our conclusions about the mechanism of this reaction.

RESULTS

Irradiation of 1-phenylbutadiene (1a) in methan[^{2}H]ol and 1-phenyl[3-^{2}H]butadiene (12) in methanol gave the products shown in Scheme 2. In each case, the *cis*- and *trans*-isomers of the diene recovered after irradiation had identical spectra to the starting compounds. The position of deuterium was deduced principally by n.m.r. evidence, the following differences being observed between spectra of labelled and unlabelled compounds: (8) has τ 7.5—7.9 (1 H, m) and 5.96 (d), whereas (3a) has τ 7.2—7.9 (2 H, m, CH$_2$) and 5.95 [t, C*H*(OMe)CH$_2$]; (9) has τ 9.3—9.9 (3 H, m), and *m*/*e* 134 (*M* − 29), whereas (5a) has τ 9.3—10.0 (4 H, m, ring CH$_2$ groups) and *m*/*e* 134 (*M* − 28) from loss of C_2H_4 by cleavage of the cyclopropane ring; (10) has no absorption around τ 6.4, whereas (6a) has τ 6.4 (q, C*H*-OMe); (11) has τ 8.74 (2 H, d) and 6.22 (q), whereas (7a) has τ 8.74 (3 H, d, CCH$_3$) and 6.22 [quintet, C*H*(OMe)CH$_3$]; (13) has no absorption at τ 4.0—4.5 and has τ 5.05br (s), whereas (3a) has τ 4.0—4.5 (1 H, C*H*=CH$_2$) and 5.04br and 5.06br (2 × s, CH=C*H*$_2$); (14) has τ 4.4—4.6 (1 H, m) and 8.30 (s), whereas (4a) has τ 4.3—4.6 (2 H, m, CH=CH) and 8.29 (d, =CH–C*H*$_3$); (16) has no absorption at τ 4.1—4.5 and has τ 4.93br (2 H, s) and 6.38 (t), whereas (6a) has τ 4.3—4.6 (1 H, m, –C*H*=CH$_2$), 4.89 and 4.93 (2 H, overlapping doublets, CH=C*H*$_2$), and 6.4 [q, C*H*(OMe)CH=CH$_2$], and (17) has no absorption around τ 6.22, and has τ 8.74 (s) and 4.03 (d), whereas (7a) has τ 6.22 (1 H, C*H*OMe), 8.74 [d, CH(OMe)C*H*$_3$], and 4.03 (dd, =C*H*–CHOMe). Too little of ether (15) was present to obtain a pure enough sample for determination of the position of deuterium.

Irradiation of 1-phenylbutadiene in acidic methanol

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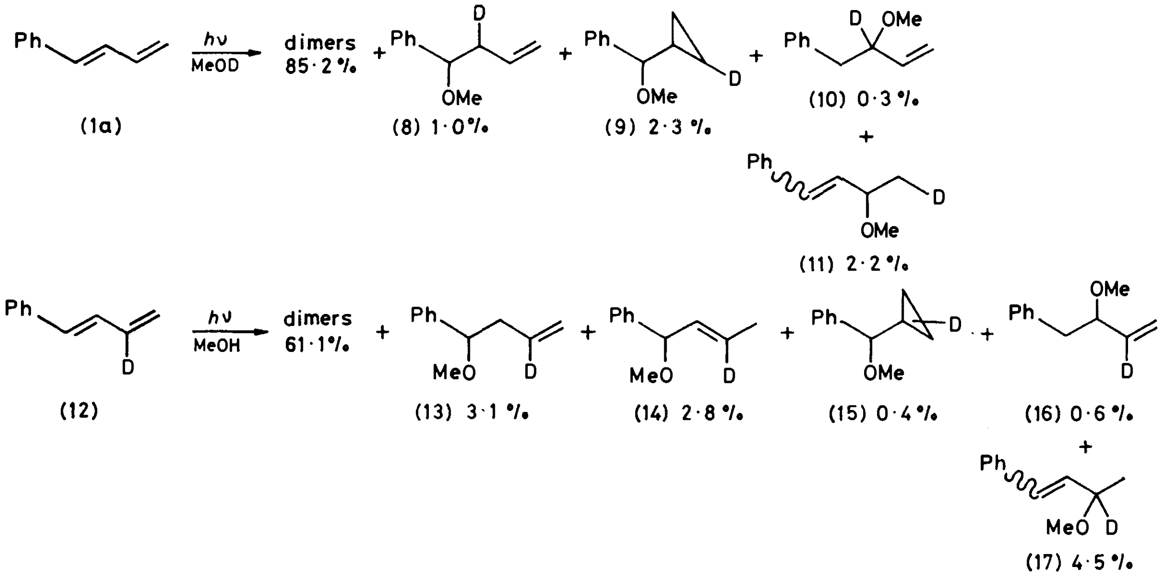
(10^{-3}M-H_2SO_4) gave the same yields of product as in neutral methanol (g.l.c. analysis). Irradiation of 1-phenylbutadiene in benzene, followed by addition of acidic methanol in the dark, gave only the cyclopropylmethyl ether (5a) in 3.2% yield (t.l.c. and g.l.c. evidence).

Results of irradiation of 1-phenylbutadiene in the presence of triplet sensitisers are shown in Table 1.

1-Arylbutadienes were found to fluoresce; fluorescence spectra and Stern–Volmer slopes for fluorescence quenching by ethanol are given in Table 2. The fluorescence of diene (1i) is comparable in intensity with that of 1,4-diphenylbutadiene, reported to have a quantum yield for fluorescence of 0.44.[8] We were unable to measure fluorescence lifetimes for any of the dienes (1a—i); in most cases the fluorescence is too weak. Some rate constants for fluorescence quenching were measured using 1,4-diphenylbutadiene, for which the fluorescence lifetime has been reported to be 0.8 ns; [8] these are given in Table 3.



SCHEME 2

TABLE 1

Sensitised irradiation of 1-phenylbutadiene

Sensitiser	E_T [a]	% Reaction	Monomeric products [b]
None		5	Trace (2a)
Acetophenone	74	68	
Benzophenone	69	79	
Anthraquinone	62	54	
Michler's ketone [c]	61	30	
Fluorenone	53	20	
Anthracene	42	93	27% (4a), 7% (7a)

[a] Triplet energy in kcal mol^{-1} from W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1964, **86**, 4537; M. R. Padhye, S. P. McGlynn, and M. Kasha, *J. Chem. Phys.*, 1956, **24**, 588; R. E. Kellogg, *ibid.*, 1966, **44**, 411. [b] Dimers were produced in all irradiations. [c] 4,4'-Bis(dimethylamino)benzophenone.

We made several measurements of the product of rate constant for diene disappearance by reaction with alcohol and singlet lifetime; results for 1-phenylbutadiene are given in Table 4. Values are small, and difficult to measure accurately. Other 1-arylbutadienes had similar values.

DISCUSSION

We previously suggested [1] that the cyclopropylmethyl ether (5) is formed by the mechanism which operates in aliphatic dienes,[4-6] namely photochemical formation of a bicyclobutane followed by thermal addition of solvent *via* bicyclobutonium ion intermediates. Our observation that dark reaction of methanol with irradiated 1-phenylbutadiene produces the ether (5a) supports this mechanism. Further support is provided by the result of irradiation in methan[^{2}H]ol (*cf.* Scheme 3).

Homoallyl products are commonly observed in solvolysis reactions involving bicyclobutonium ions,[9] and one might expect that the homoallyl ethers from 1-arylbutadienes are produced by the same mechanism as the cyclopropylmethyl ethers. (This has normally been

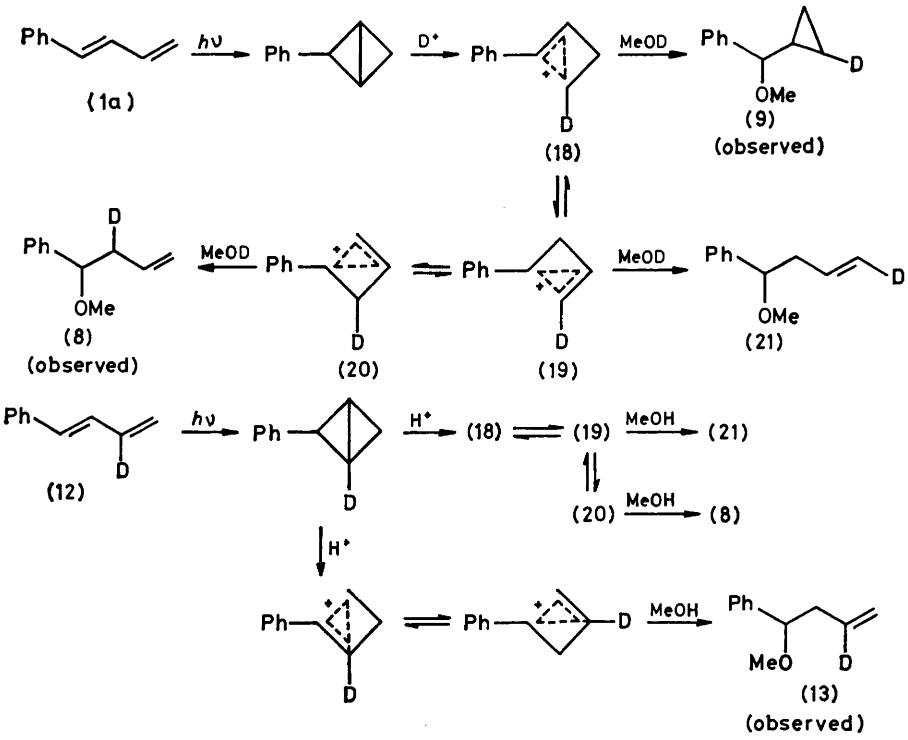
TABLE 2

1-Arylbutadiene fluorescence [a]

	Ar	$\lambda_{max.}$/nm	Intensity [b]	$k_q\tau$ [c]/ l mol^{-1}
a	Ph	340	1.0	0.154
b	3-MeC_6H_4	343	6.6	0.0293
c	4-MeC_6H_4	343	3.3	0.0352
d	2,4,6-$Me_3C_6H_2$	354	0.52	*d*
e	3-ClC_6H_4	337	34	0.0179
f	4-ClC_6H_4	341	43	<0.004
g	3-$MeOC_6H_4$	351	1 220	−0.0069
h	4-$MeOC_6H_4$	349	92	0.149
i	4-$Me_2NC_6H_4$	376	1 800	0.645
	Diene (12)	340	1.5	0.161

[a] All dienes 5 × 10^{-5}M in cyclohexane excited at absorption $\lambda_{max.}$. Emission $\lambda_{max.}$ given in nm. [b] Intensity relative to (1a) = 1.0, uncorrected for photomultiplier response. [c] Stern–Volmer slope for quenching by EtOH. [d] Fluorescence too weak to measure accurately.

assumed in aliphatic and alicyclic diene photochemistry.) However, our results show that this is not so: (i) dark reaction of methanol with irradiated diene (1a) gave no homoallyl ether (3a).* (ii) Labelling results do not support a symmetrical bicyclobutane intermediate. Predicted labelling patterns are shown in Scheme 3. In the irradiation of diene (1a) in methan[^{2}H]ol, no evidence of ether (21) was seen, implying a ratio of (8) : (21) of at least 4 : 1, which is unreasonable when no similar isotope effects have been observed in other bicyclobutonium ion rearrangements. (In the formation of 4-acetoxybut-1-ene from addition of acetic [^{2}H]acid to bicyclobutane, the 1-position is slightly favoured over the 3-position as the site of deuteriation.[6]) Similarly, the irradiation of diene (12) should yield ethers (8) and (21), but these were not observed. (iii) We have previously shown [2] that for a series of 1-arylbutadienes, the yields of homoallyl ethers (like allyl ethers) increase with electron-donating substituents, whereas there is no correlation between substituent effect and yield of cyclopropylmethyl ethers. Similarly, in the irradiation of diene (1a) in methan[^{2}H]ol and of (12) in methanol, the yields of homoallyl and cyclopropylmethyl products show no correlation.



Scheme 3

Table 3

Quenching of 1,4-diphenylbutadiene fluorescence [a]

Quencher	Et_3N [b]	MeOH	EtOH	Pr^iOH	Et_2O
$k_q\tau$/l mol^{-1}	2.88	0.205	0.224	0.205	0.068
$10^8 k_q$/l mol^{-1} s^{-1}	36	2.6	2.7	2.6	0.85

[a] Diene 10^{-5}M in benzene, excited at absorption $\lambda_{max.}$, fluorescence measured at emission $\lambda_{max.}$ [b] Hexane solution.

We therefore suggest that the homoallyl ethers from photoaddition to 1-arylbutadienes are not formed from bicyclobutanes, but by a mechanism analogous to that of allyl ether formation.

The only mechanistic studies reported for allyl ether formation involve sensitisation,[5,7] and the observation of sensitised formation of allyl ethers has been attributed to triplet [5,7] or vibrationally excited ground-state [5] intermediates. However, both reactions used aromatic hydrocarbon sensitisers and alicyclic dienes, so there are two complications to be considered: (i) sensitised *cis*–

Table 4

Effect of alcohol concentration on rate of 1-phenylbutadiene photolysis [a]

Alcohol	Solvent	[diene]/M	$10^4 k_r\tau$/ [b] l mol^{-1}
MeOH	Benzene	10^{-2}	4.5 [c]
MeOH	Benzene	10^{-2}	6.1
MeOH	Et_2O	10^{-2}	6.1
EtOH	Cyclohexane	10^{-2}	7.4
MeOH	Et_2O	10^{-3}	1.07
EtOH	Cyclohexane	10^{-3}	0.86

[a] Diene concentration as a function of time measured by u.v. absorption of *trans*-isomer, unless otherwise stated. [b] k_r is rate constant for reaction of diene with alcohol; τ is singlet lifetime of diene. [c] Diene concentration (sum of *cis*- and *trans*-isomers) measured by g.l.c.

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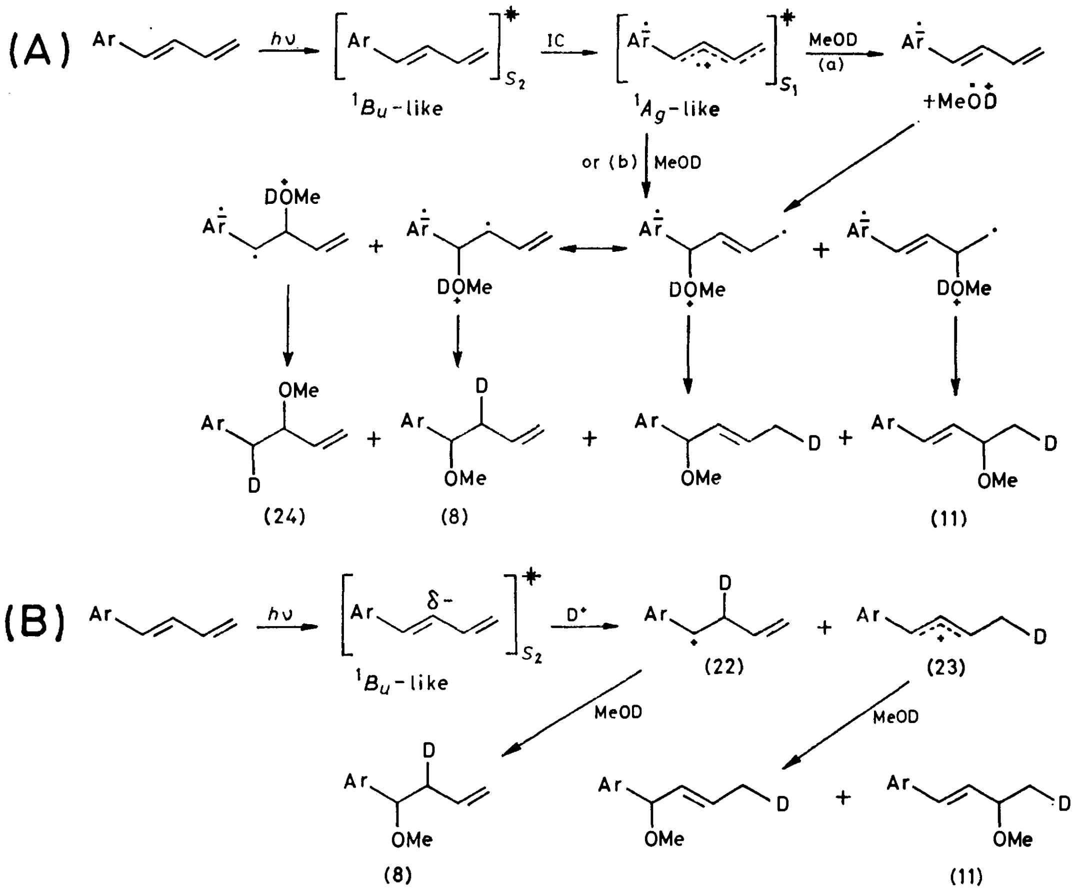
* Similar results have been reported for alicyclic dienes;[5] this evidence is not conclusive because the intermediate ions should be less stable in the less polar mixed solvent, and so give a higher proportion of the kinetically favoured product (usually the cyclopropylmethyl ether) than in pure alcohol.

trans isomerisation could result in a diene containing a *trans*-cyclohexene unit, which would readily give allyl ethers by thermal addition of methanol.[7] Such a mechanism is well established in cyclic olefin photolysis,[10] and attempted sensitisation of acyclic aliphatic dienes gives no allyl ethers with either ketone sensitisers or naphthalene.[11] (ii) Reaction may occur *via* an exciplex—exciplex emission has been observed from dienes and naphthalene or anthracene derivatives.[12] The sensitisation results reported here show that triplet energy transfer is not involved in the sensitised formation of allyl ethers, since only the lowest energy sensitiser, anthracene, was effective,* and the reaction probably involves an exciplex intermediate.[15] We conclude that allyl ether formation in direct photolysis is a singlet reaction, and follows a different mechanism from the sensitised reaction.

The observation that alcohols quench the fluorescence of 1-arylbutadienes suggests that reaction may occur directly between excited singlet diene and alcohol. Any proposed mechanism must take into account recent work on the excited states of polyenes: many calculations and experiments suggest that the lowest excited singlet state lies below the lowest spectroscopically accessible state (^1B_u in symmetrical polyenes), and has the same symmetry as the ground state (^1A_g in symmetrical polyenes).[16] We have shown that for 1-arylbutadienes the two states have very different calculated electron distributions,[16] the ^1B_u-like state having high electron-density (1.01—1.04) at C-2 of the diene group, and the ^1A_g-like state having low electron-density on the diene unit (net charge *ca.* $+0.6$ e), especially at C-1 and -4 (typical electron densities 0.8). Taking these predictions into account, two mechanisms are reasonable; these are shown in Scheme 4, where reaction with methan[^{2}H]ol has been illustrated to show predicted labelling patterns.



Scheme 4

Mechanism (A) assumes reaction in the ^1A_g-like state, which is predicted to have a diene unit susceptible to nucleophilic attack. This must lead to an intermediate with negative charge on the aryl group, either by electron transfer, path (a), or by direct nucleophilic attack, path (b). Mechanism (B), on the other hand, assumes reaction in the more nucleophilic ^1B_u-like state, implying a positively charged intermediate. Our report [2] that quantum yields of ether formation correlate with ground-state substituent constants, with negative ρ values (*ca.* -1.3 against σ, or -0.7 against σ^+), implies that the

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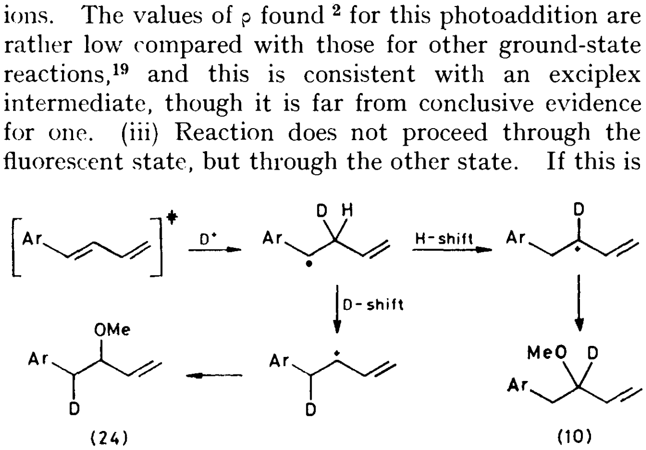
* The triplet energy of 1-phenylbutadiene is not known, but presumably lies between 42 kcal mol^{-1}, the value for 1,4-diphenylbutadiene,[13] and 60 kcal mol^{-1}, the value for butadiene.[14] The second excited triplet of anthracene is probably not involved, since acetophenone, having almost the same triplet energy, was not effective as a sensitiser.

aryl group is stabilising a positive centre in the rate-limiting step, and supports mechanism (B).

The fluorescence quenching data (Table 2) do not show a clear dependence on substituent properties,* but there are several complicating factors to be considered. We were able to measure Stern–Volmer slopes, $k_q\tau$, but not lifetimes, so we cannot estimate the rate constants, k_q. In view of the large changes in fluorescence intensity observed, one might expect rather different values of τ for the different dienes. Secondly, the Stern–Volmer slopes are small, and it was necessary to use high concentrations of ethanol to measure them accurately. The corresponding change in solvent polarity may affect the intensity of fluorescence. (This effect is presumably responsible for the negative slope observed with 3-methoxyphenylbutadiene.) Thirdly, the results in Table 3 show the composite nature of the fluorescence quenching: triethylamine and diethyl ether both quench the fluorescence of 1,4-diphenylbutadiene, presumably by electron transfer from their lone-pair orbitals. Alcohols have similar ionisation potentials to that of ether, and one would expect the rate of quenching by electron transfer to be similar (or lower, because of the loss of one electron-donating alkyl group). In fact, the rates are greater by a factor of three, implying an extra quenching mechanism, possibly hydrogen bonding or protonation. (We have observed extra quenching of 1,4-diphenylbutadiene fluorescence in methanol when sulphuric acid is added.) The quenching data in Table 2 are also likely to represent the sum of electron-transfer and protonation or hydrogen-bonding components.

If reaction occurs in the excited state to give intermediates which are converted efficiently to products, then the rate of photolysis of diene should vary with alcohol concentration, and analysis of the kinetics should lead to the same value of $k_q\tau$ as is obtained from fluorescence quenching. If k_r is the overall rate constant for reaction with alcohol, a plot of $(1 - \phi_{dis}{}^{\circ})/(1 - \phi_{dis})$ against alcohol concentration should have slope $k_r\tau$ (ϕ_{dis} is overall quantum yield for diene disappearance and $\phi_{dis}{}^{\circ}$ is ϕ_{dis} at zero alcohol concentration). Some values are shown in Table 4, and it can be seen that they are much smaller than $k_q\tau$ from fluorescence quenching. It is also apparent that the variation with change of diene concentration is outside the experimental error. This suggests that a substantial part of the measured $k_r\tau$ arises from a solvent effect on the dimerisation reaction,† and the true value for direct reaction with alcohol in the excited state cannot be reliably estimated, though it must be of the same order of magnitude as the values in Table 4. One can also estimate a value from the quantum yields of ether formation previously reported[2] of *ca.* 5×10^{-5} l mol^{-1}.

This discrepancy requires an extra step in the mechanism. There are three possibilities: (i) there is competition in the allyl and homoallyl cations between addition of solvent and loss of a proton to give the diene. This would give the required dependence on σ or σ^+ because more stable cations would be less likely to lose a proton. However, Pocker and Hill have shown[18] that acid-catalysed *cis–trans* isomerisation of 1-phenylbutadiene is slower than hydration in aqueous solution, that is, proton loss is slower than solvent addition. Although these results for cations in vibrational equilibrium need not apply to the more vibrationally excited cations which would result from protonation of excited diene, they are supported by our observation that diene recovered from irradiation in methan[^{2}H]ol does not contain deuterium in observable quantities. After addition of D^+, a kinetic isotope effect would favour loss of H^+, and one would expect appreciable deuteriation if the cations in Scheme 4 could revert to the diene. (ii) Reaction of excited diene with alcohols produces a non-fluorescent species which can readily revert to diene and alcohol. This may be an exciplex, or it may be a ground-state species, but in either case, the dependence of yields on σ or σ^+ could arise because reaction in the complex would be favoured by formation of more stable product ions. The values of ρ found[2] for this photoaddition are rather low compared with those for other ground-state reactions,[19] and this is consistent with an exciplex intermediate, though it is far from conclusive evidence for one. (iii) Reaction does not proceed through the fluorescent state, but through the other state. If this is so, fluorescence quenching is effectively a process of deactivation, reducing quantum yields, and photoaddition is a rather slower process, the rate of which is governed, to some extent, by the stability of the ground-state ion produced. In this case the calculations suggest that the ^1B_u-like state would be the one responsible for the photoaddition, implying that the lowest, fluorescent, state is ^1A_g-like.



SCHEME 5

The 4-aryl-3-methoxybut-1-ene products (6), (10), and (16) have not so far been considered. Scheme 4 shows that the expected labelling pattern (24) in mechanism (A) is not the same as is observed experimentally (10), providing further evidence against mechanism (A). If mechanism (B) is followed, a possible route to this product is shown in Scheme 5, involving a [1,2] hydrogen shift in the homoallyl cation. As shown, the alternative

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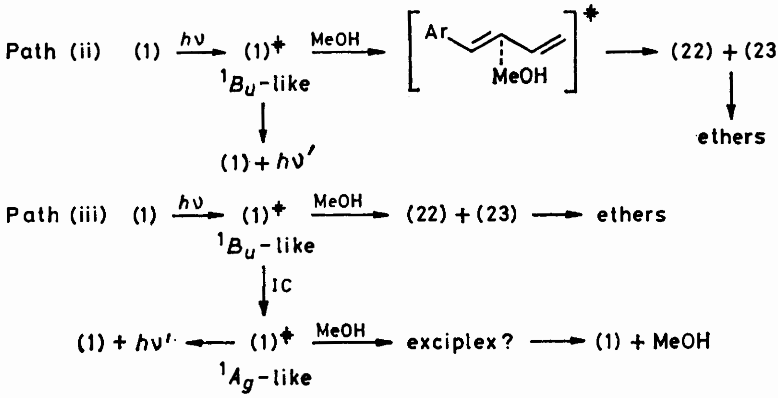
* *E.g.* correlation coefficient 0.55 for log $k_q\tau$ against σ_{ex} (values from ref. 17).

† A change in τ is a much less likely cause: there was no evidence for concentration quenching of fluorescence, and in any case τ needs to increase with increasing diene concentration to account for the observed changes. Stern–Volmer slopes for fluorescence quenching of 1,4-diphenylbutadiene by alcohols change by $<10\%$ for a change of diene concentration from 10^{-5}M to 10^{-2}M.

labelling (24) might be expected as well, but the hydrogen shift involves a weakening of a C–H bond in the transition state, and a kinetic isotope effect should favour shift of H rather than D, making (10) the main product. Since only small quantities of this ether were isolated, a small amount of (24) would not have been observed. This mechanism is consistent with the observation [2] that this type of ether is formed with electron-withdrawing substituents, which are less effective at stabilising the charge on the homoallyl cation.

We conclude that the allyl and homoallyl ethers are formed by mechanism (B) in Scheme 4, and Scheme 5, but it is necessary also to include either (a) a diene–methanol complex (probably an exciplex) before protonation occurs, or (b) a deactivation of the ^1A_g-like state, assumed to be the fluorescent state, as shown in Scheme 6.



SCHEME 6

EXPERIMENTAL

I.r. spectra were recorded with a Unicam SP 1000, u.v. spectra with a Unicam SP 800, n.m.r. spectra with Perkin-Elmer R10 (60 MHz) or R14 (100 MHz), and mass spectra with an A.E.I. MS9 or Varian CH7 spectrometer. Microanalysis was carried out by Dr. F. B. Strauss, Oxford. For analytical g.l.c. a 5 ft × 3/16 in glass column packed with 2% fluorosilicone oil FS 1265 on Embacel was used. For column chromatography Laporte type H alumina deactivated to activity III with water (4%) was used; petrol refers to light petroleum (b.p. 40—60°) freshly distilled from P_2O_5. Fluorescence spectra were recorded on an Aminco-Bowman spectrophotofluorometer.

Methan[^{2}H]ol was prepared by the method of Streitwieser *et al.*[20]

1-Phenylbutadiene (1a) was prepared and characterised as described in Part 1.[1] Other 1-arylbutadienes (1b—i) were prepared and characterised as described in Part 2.[2] Only the *trans*-isomers were used for the fluorescence measurements.

1,4-Diphenylbutadiene (Koch–Light) was recrystallised from cyclohexane.

1-Phenyl[3-^{2}H]buta-1,3-diene (12) was prepared by the dehydration of 4-phenyl[2-^{2}H]but-3-en-2-ol (4.13 g, 28 mmol) [from benzylideneacetone (4.4 g), and lithium aluminium deuteride] over potassium hydrogensulphate (0.5 g), distilling off the diene as it was formed at 15 mmHg. The distillate was dried and chromatographed on alumina, eluting with petrol, to give the ***deuteriated diene*** (64% from benzylideneacetone) (Found: C, 91.5; 4.135 mg produced 3.075 mg water. $C_{10}H_9D$ requires C, 91.6%, 2.871 mg water from 4.135 mg), $\nu_{max.}$ (film) 2 240 cm^{-1} (C-D), τ (CCl_4) 2.73 (5 H, s), 3.30 (1 H, d, *J* 15.5 Hz), 3.54 (1 H, d, *J* 15.5 Hz), 4.75 (1 H, s), and 4.90 (1 H, s), *m/e* 131 (91%, M^+), 130 (100), 129 (67), 128 (33), 116 (44), and 115 (23).

Preparative irradiations of 1-phenylbutadiene in methan[^{2}H]ol and 1-phenyl[3-^{2}H]butadiene in methanol were carred out as described in Part 2,[2] except that methan[^{2}H]ol was recovered by careful fractional distillation.

Small-scale irradiations were carried out in a Rayonet Srinivasan-Griffin reactor, RPR-100 (Southern New England Ultraviolet Co.) with a roundabout attachment MGR-100. Up to eight 10 ml samples were irradiated simultaneously using quartz tubes base-washed (2N-ammonia) before use, and deoxygenated by passing purified nitrogen for 10 min before irradiation. Most irradiations used RPR-3000 Å lamps. Where g.l.c. analysis was used, hexadecane (1—5 µl per 10 ml) was added as internal standard.

(i) Solutions of 10^{-2}M-1-phenylbutadiene in methanol, 10^{-2}M-1-phenylbutadiene in methanol containing 10^{-3}M-H_2SO_4, and 7 × 10^{-3}M-1-phenylbutadiene in benzene were irradiated for 14 h and analysed by g.l.c. 10^{-2}M-Sulphuric acid in methanol (5 ml) was added to the benzene solutions, and further g.l.c. and t.l.c. analysis carried out.

(ii) Solutions of 10^{-2}M-1-phenylbutadiene were irradiated (RPR-3500 Å lamps; 3 h) in the presence of the following sensitisers (concentration and % light absorbed by sensitiser given): none, acetophenone (10^{-2}M, 68%), benzophenone (10^{-2}M, 96%), anthraquinone (saturated, 97%), 4,4′-bis-(dimethylamino)benzophenone (10^{-2}M, >99%), fluorenone (10^{-2}M, >99.9%), pyrene (10^{-2}M, 99.8%), anthracene (saturated, 98%). Solutions were analysed by g.l.c. and, where anthracene was used, by t.l.c.

(iii) Solutions of 1-phenylbutadiene (10^{-2}M or 10^{-3}M) in methanol–benzene, methanol–ether, or ethanol–cyclohexane (alcohol concentrations 0, 5, 10, 20, 40, 60, and 89%) were irradiated and analysed by g.l.c. or u.v. In each case, an actinometer solution of 0.1M-benzophenone and 0.1M-diphenylmethanol in benzene was also irradiated (ϕ for disappearance of benzophenone taken as 0.67 [21]). For g.l.c. analysis, irradiation times were 5.5 and 10 h; for u.v. analysis, irradiation times were 30 min (10^{-2}M-diene) and 15 min (10^{-3}M-diene). All u.v. analyses used difference spectra of the same solution before and after irradiation, relative to a base-line recorded with 5 × 10^{-4}M-diene in both cells. Similar irradiations of other 1-arylbutadienes (10^{-3}M) in ethanol–cyclohexane mixtures gave similar results.

Fluorescence Measurements.—Fluorescence spectra of 1-phenylbutadiene and 1,4-diphenylbutadiene were measured at concentrations from 10^{-7} to 10^{-2}M. No evidence was seen of concentration quenching, or excimer formation. The concentration giving maximum fluorescence (due to the inner filter effect) was used in most quenching studies, though some quenching studies at much higher concentrations were carried out to check for variation of k_q with diene concentration. No deoxygenation was carried out, since passing nitrogen had little effect on the fluorescence of the dienes, but increased the background fluorescence of the solvents. Quenching of fluorescence of 1-arylbutadienes (see Table 2) used 5 × 10^{-5}M-*trans*-diene in cyclohexane containing 0—50% ethanol, excited at the absorption maximum. Quenching of the fluorescence of 1,4-diphenylbutadiene used 10^{-5}M-diene in benzene or hexane containing 0—60% triethylamine, methanol, ethanol, propan-2-ol, or diethyl ether (freshly distilled from $LiAlH_4$ under nitrogen); some studies with 10^{-2}M-diene in benzene containing 0—50% methanol or ethanol gave essentially the same results.

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