

Photochemistry of Arylbutadienes. Part 2.¹ Preparation and Photochemistry of 1-(Substituted-aryl)butadienes. A Ground-state Substituent Effect on an Excited-state Reaction

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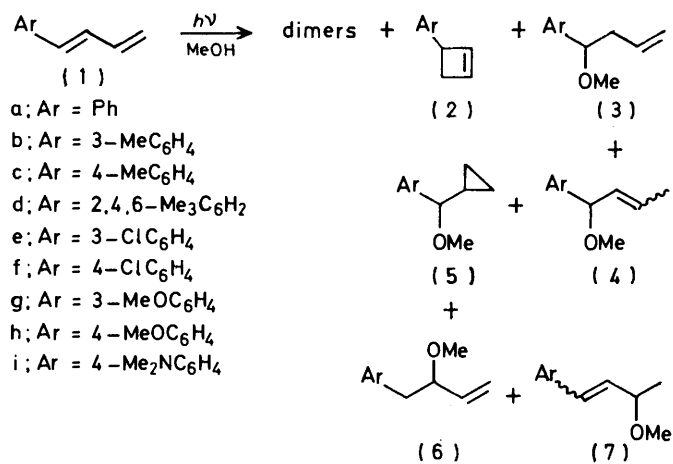
Yields and quantum yields are reported for the photoaddition of methanol to 1-phenylbutadiene and eight substituted 1-phenylbutadienes. For allyl and homoallyl products $\log \phi$ correlates more satisfactorily with ground-state substituent constants than with excited-state constants; for cyclopropylmethyl products, no correlation is observed with either set of constants.

THE Hammett equation and related equations involving substituent constants have become established as a technique for mechanistic study of ground-state reactions, but have found relatively little use in the study of photochemical reactions. Recently, we reported² an analysis of singlet excited-state reactivity data, leading to a new set of substituent constants, σ_{ex} , which were shown to correlate excited-state reactivity more consistently than the Hammett constants, σ . We now report the first application of the new constants to provide evidence about the mechanism of a photochemical reaction.

The reaction studied is the formation of methyl ethers from photoaddition of methanol to 1-arylbutadienes (Scheme), which was reported in Part 1.¹ This reaction is analogous to the corresponding reaction of aliphatic and alicyclic dienes, in which the mechanism of formation of cyclopropylmethyl ethers is well established, but that for formation of allyl and homoallyl ethers is still uncertain.³

RESULTS

Nine 1-arylbutadienes were irradiated; the products are shown in the Scheme. Evidence for the structures of the products of 1-phenylbutadiene (1a) was given previously;¹ the products of the other dienes (1b–i) were identified by the similarity of their spectra to those of the 1-phenylbutadiene photoproducts, the only differences being those expected from the electron-donating or -withdrawing effect



SCHEME

of the substituents, and the substitution pattern of the benzene ring. Yields and approximate quantum yields are given in Tables 1 and 2. A 3-arylcyclobutene (2) was

TABLE 1

Yield of 1-arylbutadiene photoproducts^a

Diene	% Dimer	% (3)	% (4)	% (5)	% (6)	% (7)
(1a)	51.0	2.8	4.2	2.0	0.8	4.2
(1b)	69.8	3.3	—	—	—	12.1
(1c)	60.0	6.4	7.6	1.1	—	13.3
(1d)	22.4	12.5	11.1	0.5	—	25.4
(1e)	65.6	—	—	1.0	—	4.0
(1f)	86.5	1.5	—	0.7	0.3	3.9
(1g)	83.0	1.1	1.9	—	1.0	2.1
(1h)	10.3	5.3	24.4	—	—	20.4
(1i)	8.5	<i>b</i>	30.0	—	—	50.8

^a Based on conversion, from n.m.r. analysis of column fractions. Irradiation to 85% conversion. For ethers (4) and (7), combined yield of *cis*- and *trans*-isomers is given. A dash indicates less than 0.5%. ^b This product is not stable to chromatography.

TABLE 2

Quantum yields of 1-arylbutadiene photolysis

Diene	ϕ_{dis} ^a	(3)	(4)	$10^4 \phi_t$ ^b (5)	(6)	(7)
(1a)	0.0121	3.4	5.1	2.4	1.0	5.0
(1b)	0.0115	3.8	—	—	—	13.9
(1c)	0.0108	6.9	8.2	1.2	—	14.3
(1e)	0.0092	—	—	0.9	—	3.6
(1f)	0.0131	2.0	—	0.9	0.4	5.1
(1g)	0.0237	2.6	4.5	—	2.4	5.0
(1h)	0.0109	8.6	26.6	—	—	22.2
(1i)	0.0247	—	74.1	—	—	126

^a Quantum yield for diene disappearance. ^b Quantum yield for product formation.

observed only in the irradiation of 1-phenylbutadiene (1a). The figures quoted for dimers include all unidentified hydrocarbons; some unidentified ethers were also produced in small quantities (0–2% total). The remaining material was insoluble polymer on the irradiation vessel. In the irradiation of 4-dimethylaminophenylbutadiene (1i), t.l.c. of the crude photoproduct mixture showed the presence of homoallyl ether (3i), although this was not isolated from the column.

DISCUSSION

It is difficult to make a quantitative estimate of the errors in the quantum yields of product formation ϕ_t .

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The yields of product in Table 1 were calculated from the weight of each of the column fractions from the photo-product mixture and its composition, as determined by n.m.r. and g.l.c., and were checked by g.l.c. analysis of the crude mixture from the irradiation.* Recovery of material in distillation and chromatography was 95% or better, and taking this into account, together with errors in weighing and n.m.r. and g.l.c. analysis, the error in the yields is believed to be *ca.* 10%. The absolute values of the quantum yields ϕ_f may be quite unreliable, since they are calculated from the quantum yield for diene disappearance and the product yields measured under different irradiation conditions. However, for the reactivity correlations, the relative values are more important, and these should be more reliable since the same conditions were used for all dienes. For several measurements of ϕ_{dis} for 1-phenylbutadiene, the standard deviation was *ca.* 5%, and we take this to be the error in the values of ϕ_{dis} in Table 2. Thus the total estimated error in the quantum yields ϕ_f is *ca.* 15%, which corresponds to an error of *ca.* 0.07 in $\log \phi_f$.

Table 3 shows the results of a least-squares analysis of the linear relation between $\log \phi_f$ and the substituent

TABLE 3

Correlations of $\log \phi_f$ with substituent constants ^a

Ether	Constants ^b	ρ	r	S.d.
(3)	σ	-1.32	0.982	0.052
	σ^+	-0.67	0.922	0.106
	σ_{ex}	-1.04	0.855	0.141
(4)	σ	-1.36	0.956	0.177
		(-1.86)	(0.905)	(0.184)
	σ^+	-0.71	0.987	0.097
(7)		(-0.92)	(0.994)	(0.047)
	σ_{ex}	-2.01	0.949	0.136
	σ	-1.34	0.972	0.130
(4) + (7) ^c		(-1.24)	(0.911)	(0.138)
	σ^+	-0.74	0.970	0.135
		(-0.74)	(0.897)	(0.148)
(4) + (7) ^c	σ_{ex}	-1.26	0.807	0.197
	σ	-1.51	0.988	0.096
		(-1.65)	(0.974)	(0.095)
(4) + (7) ^c	σ^+	-0.83	0.982	0.115
		(-1.0)	(0.973)	(0.097)
	σ_{ex}	-1.80	0.923	0.161

^a The least-squares correlation coefficient is r , s.d. is the standard deviation of $\log \phi_f$ from the correlation line. Figures in parentheses are calculated omitting values for the dimethylamino-substituent. ^b σ and σ^+ from C. Laurence and B. Wojtkowiak, *Ann. Chim. (France)*, 1970, **5**, 163; σ_{ex} from ref. 2. ^c Total quantum yield of allyl ether formation.

constants σ , σ^+ , and σ_{ex} . Since no σ_{ex} value is available for the dimethylamino substituent, correlations with σ and σ^+ are also given omitting this substituent. Only the homoallyl ether (3) and the allyl ethers (4) and (7) are shown because the other two ethers do not show any significant correlation with any set of substituent constants.

Comparison of the correlation coefficients shows that, in general, σ_{ex} gives the worst correlation. It is only with ether (4) when the dimethylamino-substituent is omitted that the correlation coefficient for σ_{ex} is less than

* It was not possible to use g.l.c. analysis alone because some ethers could not be separated satisfactorily.

that for σ . A more significant comparison uses the standard deviation of $\log \phi_f$ from the correlation lines. If the linear relationship is valid, then the standard deviations should be comparable with the experimental error in $\log \phi_f$. (Standard deviations much less than the experimental error are probably fortuitous.)

For the homoallyl ethers (3), correlations with σ and σ^+ have standard deviations comparable with experimental error, the correlation with σ appearing more satisfactory. The correlation with σ_{ex} has rather greater standard deviation, and it is clear that ground-state constants are more satisfactory for this type of product.

For allyl ethers (4) and (7), the only satisfactory correlation is between ether (4) and σ^+ . However, these two ethers (4) and (7) are readily interconvertible by allylic rearrangement, and a measure of the quantum yields of formation of the corresponding allylic cation can be obtained by taking the total quantum yield for the two ethers. Correlation data for this are also given in Table 3, and it can be seen that both σ and σ^+ give standard deviations comparable with experimental error, whereas σ_{ex} still gives an unsatisfactory correlation.

We may also consider some qualitative comparisons. Previously,² we pointed out the extra electron-donating effect of *m*-substituents in the excited state; thus 3-methoxy ($\sigma_{ex} - 0.10$) is electron donating, and 3-chloro ($\sigma_{ex} 0.10$) is less electron withdrawing than 4-chloro ($\sigma_{ex} 0.23$). These are the opposite of the ground-state effects. Table 2 shows that, in general, ϕ_f increases with increasing electron-donating character of the substituent, but lower quantum yields of ethers (3) and (4) are obtained with 3-methoxy than with the unsubstituted diene and lower quantum yields of ethers (3) and (7) were obtained with 3-chloro than with 4-chloro. Both comparisons are in qualitative agreement with ground-state substituent constants but not with σ_{ex} .

We therefore conclude that the formation of products (3), (4), and (7) in the irradiation of 1-arylbutadienes correlates with ground-state substituent constants σ or σ^+ rather than with the excited-state constants σ_{ex} . This suggests that the rate-limiting or product-determining steps are controlled by free energies or activation energies of ground-state species. Unfortunately, the data are not accurate enough to distinguish between σ and σ^+ , though it should be noted that the correlation coefficient between σ and σ^+ is 0.976 for the substituents used in this study, and it would, therefore, be difficult to distinguish between them. The negative values of ρ imply that stabilisation of positive charge is important; a more detailed discussion of the mechanism is given in the following paper.⁴

EXPERIMENTAL

I.r. spectra were recorded with a Unicam SP 1000, u.v. spectra with a Unicam SP 800, or, where indicated, a Cary 14M, 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 \times 3/16-in glass column packed with 2% fluorosilicone oil FS 1265 on Embacel was used. For column chromatography Laporte type H alumina was used, deactivated to activity III with 4% water or to activity IV—V with 10% water; petrol refers to light petroleum (b.p. 40—60°), freshly distilled from P₂O₅.

Preparation of Dienes.—1-Phenylbutadiene (1a) was prepared and characterised as described in Part 1.¹

1-(3-Methylphenyl)buta-1,3-diene⁵ (1b) was purified by chromatography on alumina (4% water) eluting with petrol (Found: C, 91.3; H, 8.2. Calc. for C₁₁H₁₂: C, 91.6; H, 8.4%), ν_{\max} (film) 3 050, 3 020, 1 637, 1 608, 1 002, 968, 910, 785, and 701 cm⁻¹, τ (CCl₄) 2.6—3.2 (4 H, m), 3.2—3.8 (3 H, m), 4.75 (1 H, d, J 18 Hz), 4.89 (1 H, d, J 9.5 Hz), and 7.69 (3 H, s), λ_{\max} (cyclohexane) 213 (ϵ 15 000), 222.5 (13 300), 229 (13 300), 236 (9 300), 275 (24 000), 283 (25 300), and 310 nm (4 000), *m/e* 144 (51%, M⁺), 130 (13), 129 (100), 128 (76), 127 (21), and 115 (23).

1-(4-Methylphenyl)buta-1,3-diene⁵ (1c) was purified by chromatography on alumina (4% water) eluting with petrol (Found: C, 91.2; H, 8.8. Calc. for C₁₁H₁₂: C, 91.6; H, 8.4%), ν_{\max} (film) 3 080, 3 020, 3 000, 1 635, 1 601, 1 006, 954, 903, 869, and 810 cm⁻¹, τ (CCl₄) 2.88 (4 H, ragged q), 3.2—4.0 (3 H, m), 4.6—5.1 (2 H, m), and 7.71 (3 H, s), λ_{\max} (cyclohexane) 209 (ϵ 13 000), 213 (14 300), 221 (12 400), 227 (11 900), 235 (8 300), 276 (26 200), 283 (27 600), and 310 nm (6 600), *m/e* 144 (37%, M⁺), 129 (100), 128 (74), 127 (23), 115 (21), and 91 (13).

1-(2,4,6-Trimethylphenyl)but-2-en-1-ol was prepared by addition of crotonaldehyde (7 g, 0.1 mol) to mesitylmagnesium bromide [from magnesium (3.6 g, 0.15 mol) and bromomesitylene (19.9 g, 0.1 mol), started by adding bromoethane]. After stirring overnight, the mixture was added to 4M-ammonium chloride and filtered through Whatman 1 PS paper. The ethereal filtrate was dried (K₂CO₃), evaporated, distilled, and the distillate recrystallised (petrol) to give the *enol* (20%), b.p. 98—103° at 0.2 mmHg, m.p. 60—61° (Found: C, 82.0; H, 9.6. C₁₃H₁₈O requires C, 82.1; H, 9.5%), ν_{\max} (film) 3 430, 3 030, 1 672, 973, and 859 cm⁻¹, τ (CCl₄) 3.35 (2 H, s), 4.1—4.9 (3 H, m), 7.77 and 7.82 (10 H overall, ragged s), and 8.36 (3 H, d, J 4.5 Hz).

1-(2,4,6-Trimethylphenyl)buta-1,3-diene (1d) was prepared by dehydration of 1-(2,4,6-trimethylphenyl)but-2-en-1-ol (3 g, 16 mmol) by potassium hydrogensulphate (*ca.* 0.5 g), distilling the product as it formed at 0.05 mmHg. The distillate was chromatographed on alumina (4% water) eluting with petrol to give the diene (79%) (Found: C, 90.3; H, 9.9. Calc. for C₁₃H₁₆: C, 90.6; H, 9.4%), ν_{\max} (film) 3 080, 3 040, 3 010, 1 642, 1 613, 1 603, 1 376, 1 007, 956, 906, 864, and 852 cm⁻¹, τ (CCl₄) 3.26 (2 H, s), 3.4—4.1 (3 H, m), 4.6—5.2 (2 H, m), and 7.74 (9 H, s), λ_{\max} (cyclohexane) 219 (ϵ 22 300) and 270 nm (16 700), *m/e* 172 (25%, M⁺), 157 (100), 143 (17), 142 (98), 141 (45), 129 (21), 128 (25), and 115 (30).

Allyltriphenylphosphonium bromide was prepared from equimolar amounts of triphenylphosphine and allyl bromide in benzene. The phosphonium salt was collected, washed, dried, and used without further purification.

Diene Preparation by the Wittig Reaction.—Allyltriphenylphosphonium bromide (38.3 g, 0.1 mmol) and the arenecarbaldehyde (0.1 mmol) were dissolved in ethanol (100 ml) with a trace of *N*-phenyl-2-naphthylamine, and nitrogen was passed. Lithium ethoxide [from lithium (0.76 g, 0.11

mol)] in ethanol (50 ml) was added, giving an intense green colour, which changed to red-brown when reaction was complete; the progress of the reaction was checked by t.l.c. The mixture was poured into water, extracted with petrol, and the extracts chromatographed on alumina, eluting with petrol. The products were mixtures of *cis*- and *trans*-isomers; the *trans*-isomer was obtained by irradiating the diene (200 mg, *cis-trans* mixture) in petrol (10 ml) with a few crystals of iodine for 2 min with a 100-W tungsten lamp. Passing the solution through a short alumina column, and evaporation, gave the pure *trans*-diene.

1-(3-Chlorophenyl)buta-1,3-diene (1e) was prepared by the Wittig reaction (3—4 min). The diene (25%) was chromatographed on alumina (4% water), then passed through a short column of silica, eluting with petrol, to remove a by-product, probably 3-chlorobenzaldehyde diethyl acetal (n.m.r. evidence) (Found: C, 72.1; Cl, 21.5. C₁₀H₉Cl requires C, 72.9; Cl, 21.6%), ν_{\max} (film) 3 080, 3 050, 3 020, 1 598, 1 092, 1 078, 1 003, 912, 888, 801, 780, 741, and 694 cm⁻¹, τ (CCl₄) 2.5—2.9 (4 H, m), 3.1—4.0 (3 H, m), and 4.4—5.0 (2 H, m), λ_{\max} (*trans*-isomer, cyclohexane) 217 (ϵ 16 700), 224 (15 800), 231 (15 900), 238 (11 700), 275 (26 400), 281 (27 000), and 314 nm (2 900), *m/e* 166 (5%, ³⁷Cl M⁺), 164 (12, ³⁵Cl M⁺), 129 (100), 128 (57), and 127 (30).

1-(4-Chlorophenyl)buta-1,3-diene (1f) was prepared by the Wittig reaction (2—3 min). The diene (14%) was chromatographed on alumina (4% water) (Found: C, 72.7; H, 5.7; Cl, 21.2. Calc. for C₁₀H₉Cl: C, 72.9; H, 5.5; Cl, 21.6%), ν_{\max} (film) 3 080, 3 020, 3 010, 1 631, 1 603, 1 092, 1 057, 1 013, 1 004, 951, 912, 869, 848, 817, and 653 cm⁻¹, τ (CCl₄) 2.75br (4 H, s), 3.0—4.1 (3 H, m), 4.4—5.0 (2 H, m), λ_{\max} (*trans*-isomer, cyclohexane) 213 (ϵ 15 000), 219 (12 500), 226 (10 900), 233 (6 600), 280 (30 900), 285 (31 700), and 312 nm (6 600), *m/e* 166 (6%, ³⁷Cl M⁺), 164 (17, ³⁵Cl M⁺), 129 (100), 128 (61), 127 (37), and 77 (20).

1-(3-Methoxyphenyl)buta-1,3-diene (1g) was prepared by the Wittig reaction (5 min). The diene (20%) was chromatographed on alumina (4% water) (Found: C, 82.4; H, 7.7. C₁₁H₁₂O requires C, 82.5; H, 7.6%), ν_{\max} (film) 3 080, 3 040, 3 020, 3 010, 2 840, 1 636, 1 611, 1 600, 1 275, 1 162, 1 052, 1 010, 952, 911, 782, and 700 cm⁻¹, τ (CCl₄) 2.6—4.1 (7 H, m), 4.5—5.1 (2 H, m), and 6.24 (3 H, s), λ_{\max} (*trans*-isomer, cyclohexane) 222 (ϵ 16 000), 228 (15 400), 235 (13 400), 238 (9 400), 279 (24 400), 280 (18 700), 309 (6 800), and 323 nm (3 200), *m/e* 160 (100%, M⁺), 159 (68), 145 (33), 144 (48), 129 (63), 128 (43), 127 (32), 117 (39), 116 (27), 115 (63), and 91 (32).

1-(4-Methoxyphenyl)buta-1,3-diene (1h) was prepared by the Wittig reaction (6 h). The diene (32%) was chromatographed on alumina (no added water) eluting with 10% ether-petrol (Found: C, 82.2; H, 7.5. Calc. for C₁₁H₁₂O: C, 82.5; H, 7.6%), ν_{\max} (film) 3 120, 3 060, 3 040, 2 870, 1 644, 1 619, 1610, 1 266, 1 186, 1 046, 1 012, 913, 874, 856, and 833 cm⁻¹, τ (CCl₄) 2.6—4.2 (7 H, m), 4.5—5.1 (2 H, m), and 6.28 (3 H, s), λ_{\max} (*trans*-isomer, hexane, Cary 14M), 220.5 (ϵ 13 300), 226 (11 300), 233.5 (6 000) and 288 nm (26 800), *m/e* 160 (100%, M⁺), 159 (68), 145 (30), 144 (50), 129 (55), 128 (34), 118 (52), 116 (65), and 91 (60). The *trans*-isomer was also obtained on recrystallisation from aqueous methanol, m.p. 50—51° (lit.,⁵ 46°).

1-(4-Dimethylaminophenyl)buta-1,3-diene (1i) was prepared by the Wittig reaction (30 min). The diene (27%) was chromatographed on alumina (4% water) eluting with 5% ether-petrol (Found: C, 83.3; H, 8.3; N, 7.8. C₁₂H₁₅N requires: C, 83.2; H, 8.7; N, 8.1%), ν_{\max} (Nujol)

3 080, 1 611, 997, 946, 898, 888, 858, 828, and 809 cm^{-1} , τ (CCl_4) 2.7—3.05 (2 H, ragged q), 3.1—4.3 (5 H, m), 4.6—5.2 (2 H, m), and 7.10 (6 H, s), λ_{max} (*trans*-isomer, cyclohexane) 235 (ϵ 13 600) and 321 nm (30 000), m/e 173 (100%, M^+), 172 (98), 158 (21), 157 (67), 129 (43), and 128 (33).

The 1-arylbutadienes are sensitive to air and traces of acid, and polymerise readily, especially the 4-chlorophenyl and 4-dimethylaminophenyl dienes. All dienes were stored at -40° under nitrogen, and purified immediately before use by passing through a short column of alumina, eluting with petrol.

Preparative Irradiations.—The 1-arylbutadiene (5—10 mmol) in methanol (250 ml) was irradiated in an immersion reactor, using a Hanovia 450-W medium-pressure mercury-arc lamp filtered through quartz. The apparatus was base-washed before use with 2M-ammonia,* and purified nitrogen was passed during irradiation. The progress of the reaction was followed by g.l.c., t.l.c., and u.v., and the irradiation was stopped when *ca.* 85% of the diene had disappeared (*ca.* 1—6 h). (At higher conversion than 90—95%, the allyl ethers are further photolysed.) The photoproduct mixture was evaporated and bulb-distilled, bath temperature 50—150° at 15 mmHg (1-phenylbutadiene), 1 mmHg (1-tolylbutadienes), or 0.1 mmHg (other dienes). Residue and distillate were weighed to check for loss of material (typically <10 mg), and analysed by g.l.c. to check for changes in composition and to check that the residue contained no monomeric material. The distillate was chromatographed on alumina (150 g, 4% water), eluting with petrol and 2—5% ether-petrol. Photoproduct mixtures from 4-methoxyphenyl- and 4-dimethylaminophenyl-substituted dienes contained relatively little dimer (g.l.c. evidence), and were not distilled, but the crude photoproduct after evaporation was chromatographed on alumina (150 g, 10% water), eluting with petrol and 2—10% ether-

* We have previously found this to be necessary to obtain reproducible results when irradiating aliphatic dienes.

petrol. Fractions with the same t.l.c. behaviour were combined, evaporated, weighed, and analysed by n.m.r. and g.l.c. The ethers (3)—(7) were identified by the similarity of their spectra to those with Ar = phenyl. Dimers were identified by their characteristic broad bands in the n.m.r. spectrum, and their long g.l.c. retention times. Figures in Table 2 for % dimers include the distillation residue and any other unidentified hydrocarbons.

Quantum Yield Measurement.— 10^{-2} M-Solutions of 1-arylbutadienes in methanol (10 ml) were deoxygenated by passing purified nitrogen for 10 min, then irradiated at 300 nm (Rayonet reactor RPR-100, roundabout attachment MGR-100, RPR-3000 Å lamps) in quartz tubes for 30 min, then a further 3.5 h. Samples at these times were diluted by a factor of 25 and their u.v. spectra measured. (The equilibrium *cis-trans* ratio is reached by 30 min.) An actinometer solution of 0.1M-benzophenone and 0.1M-diphenylmethanol in benzene (quantum yield for benzophenone disappearance ϕ 0.67) was irradiated simultaneously for the first 30 min, and also analysed by u.v. The quantum yield for diene disappearance was calculated from the change in u.v. absorbance of diene over the final 3.5 h, compared with the change of u.v. absorbance of benzophenone; a series of test runs with 1-phenylbutadiene showed this procedure to be reproducible to within 5%. Quantum yields for product formation were calculated from quantum yields for diene disappearance and chemical yields for product formation.

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