Photocyclization reactions of aryl polyenes. The photocyclization of 1-substitutedphenyl-4-phenyl-1,3-butadienes

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Irradiation of 1-*p*-substitutedphenyl-4-phenyl-1,3-butadienes gave mixtures of 1-*p*-substitutedphenylnaphthalenes and 7-substituted-1-phenylnaphthalenes. Photocyclization of 1-*m*-substitutedphenyl-4-phenyl-1,3-butadienes gave 1-*m*-substitutedphenylnaphthalenes, 6-substituted-1-phenylnaphthalenes, and 8-substituted-1-phenylnaphthalenes. Characterization of the photoproducts was achieved through synthesis by an independent method.

The photochemical *cis–trans* isomerization of stilbenes has been extensively investigated in recent years and the detailed mechanism of the reaction has been discussed by several groups (1). The concurrent photochemical cyclizations of stilbene and substituted stilbenes to phenanthrene and substituted phenanthrenes have also been studied both from preparative (2) and mechanistic (3) points of view.[1] Stilbene-like photochemical cyclizations have recently been utilized in the synthesis of a wide variety of interesting polycyclic compounds (4).

Photochemical cyclizations[1] of 1,4-diphenyl-1,3-butadienes have received scant attention since Fonken showed that 1,4-diphenyl-1,3-butadiene undergoes a photochemical cyclization to give 1-phenylnaphthalene (5). The present paper describes the photocyclization of 1-substitutedphenyl-4-phenyl-1,3-butadienes.

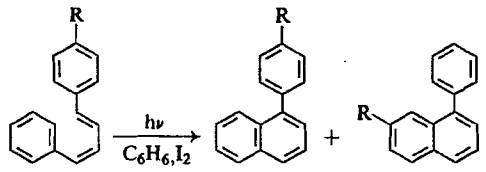
The 1-substitutedphenyl-4-phenyl-1,3-butadienes (**1***a–e* and **2***a–e*) were prepared by one of two possible Wittig reactions (6). Either a solution of triphenylcinnamylphosphonium bromide and a monosubstituted benzaldehyde in methanol was reacted with lithium methoxide (method A) or a solution of cinnamaldehyde and a monosubstitutedbenzylphosphonium halide in methanol was treated with lithium methoxide (method B). Although the yields of these reactions were only moderate (Table 1), the ready availability of the starting materials and the simplicity of the reactions favored the use of Wittig reactions in the synthesis of 1,4-diaryl-1,3-butadienes.

[1]The photochemical cyclization reaction of stilbenes gives dihydrophenanthrene intermediates, which are very readily oxidized to phenanthrenes. Hence the term "photocyclization" shall include both the cyclization and oxidation steps.

Compounds **1***a–e* and **2***a–e* were readily characterized by their spectral data (Table 2) and by comparison with known 1,4-diaryl-1,3-butadienes. Mass spectroscopy revealed the presence of strong parent ions for **1***a–e* and **2***a–e*. The ultraviolet (u.v.) and infrared (i.r.) spectra clearly showed the presence of the butadiene moiety.[2]

Irradiation of 1×10^{-3} *M* solutions of 1-*p*-substitutedphenyl - 4 - phenyl - 1,3 - butadienes (**1***a–e*) in dry benzene containing 2×10^{-3} *M* iodine gave, after 3–6 days, mixtures of 1-*p*-substitutedphenylnaphthalenes (**3***a–e*) and 1-phenyl-7-substitutednaphthalenes (**4***a–e*). As shown in eq. [1], photocyclization of **1***a–e* can occur to the unsubstituted phenyl ring to give **3***a–e* and to the substituted phenyl ring to give **4***a–e*.

[1]



1	3	4
a R = MeO	*a* R = MeO	*a* R = MeO
b R = Me	*b* R = Me	*b* R = Me
c R = Cl	*c* R = Cl	*c* R = Cl
d R = F	*d* R = F	*d* R = F
e R = CN	*e* R = CN	*e* R = CN

Similarly, irradiation of 1 - *m* - substituted - phenyl-4-phenyl-1,3-butadienes (**2***a–e*) gave mixtures of 1-*m*-substitutedphenylnaphthalenes (**5***a–e*), 1-phenyl-6-substitutednaphthalenes (**6***a–e*),

[2]It is assumed that the *trans–trans* butadienes are formed from the method of preparation and the i.r. spectral data of **1***a–e* and **2***a–e* show absorption peaks for *trans* double bonds.

TABLE 1

1-Substitutedphenyl-4-phenyl-1,3-butadienes

Compound	Substituent	Melting point (°C)	Method of synthesis	Yield (%)	Molecular formula	Analysis (%) Found C	Found H	Calculated C	Calculated H
1*a*	*p*-Methoxy	163–164	A	54	$C_{17}H_{16}O$	86.61	6.73	86.41	6.82
1*b*	*p*-Methyl	155–156*	B	50	$C_{17}H_{16}$	—	—	—	—
1*c*	*p*-Chloro	166–167†	A	46	$C_{16}H_{13}Cl$	—	—	—	—
1*d*	*p*-Fluoro	154–155	A	26	$C_{16}H_{13}F$	85.96	5.79	85.72	5.83
1*e*	*p*-Cyano	164–165‡	B	34	$C_{17}H_{13}N$	—	—	—	—
2*a*	*m*-Methoxy	78–79	A	16	$C_{17}H_{16}O$	86.15	6.66	86.41	6.82
2*b*	*m*-Methyl	102–103§	B	38	$C_{17}H_{16}$	—	—	—	—
2*c*	*m*-Chloro	113–114‖	A	29	$C_{16}H_{13}Cl$	—	—	—	—
2*d*	*m*-Fluoro	111–112	A	24	$C_{16}H_{13}F$	85.48	5.77	85.75	5.83
2*e*	*m*-Cyano	115–116	B	43	$C_{17}H_{13}N$¶	88.01	5.99	88.28	5.62

*Lit. (19), m.p. 156°.
†Lit. (20); m.p. 161°.
‡Lit. (21), m.p. 162–163°.
§Lit. (22), m.p. 95–96.5°.
‖Lit. (20), m.p. 114°.
¶Anal. Calcd.: N, 6.06. Found: N, 6.31.

TABLE 2

Spectral characteristics of 1-substitutedphenyl-4-phenyl-1,3-butadienes

Compound	Substituent	Ultraviolet spectra λ_{max}(nm)(ε)			Infrared spectra ν(cm^{-1})	Mass spectra *m/e*, M^+ (% of base peak)
1*a*	*p*-Methoxy	361 (30 500)	342.5 (44 700)	331 (37 500)	—	236 (100)
1*b*	*p*-Methyl	355 (33 800)	337 (54 200)	323 (47 000)	1610, 1020	220 (95)
1*c*	*p*-Chloro	351 (33 400)	336 (53 100)	325 (44 000)	1590, 998	240 (97)
1*d*	*p*-Fluoro	351 (23 500)	332.5 (38 900)	319 (35 000)	1600, 1240, 1160, 991	224 (100)
1*e*	*p*-Cyano	365 (27 100)	347.5 (40 800)	335 (34 200)	2235, 1601, 998	231 (100)
2*a*	*m*-Methoxy	354 (26 100)	337.5 (40 000)	326 (35 400)	1592, 1570, 1157, 992	236 (100)
2*b*	*m*-Methyl	355 (24 300)	335 (39 500)	322.5 (35 400)	—	220 (100)
2*c*	*m*-Chloro	353 (30 200)	335 (48 600)	322 (41 700)	1590, 1562, 994	240 (93)
2*d*	*m*-Fluoro	351.5 (32 100)	333 (48 900)	322 (40 000)	1600, 1256, 1150, 989	224 (81)
2*e*	*m*-Cyano	353 (28 100)	335 (43 100)	326 (39 700)	2280, 1615, 1580, 1010	231 (100)

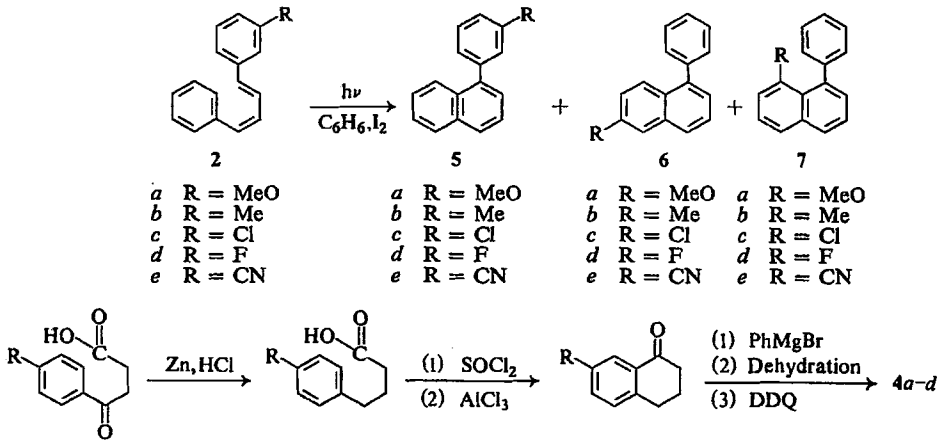
and 1-phenyl-8-substitutednaphthalenes (**7***a–e*). Photocyclization of **2***a–e* can thus occur to the unsubstituted phenyl ring to give **5***a–e* and to the substituted ring to give **6***a–e* and **7***a–e* (eq. [2]).

The photochemical reactions of **1***a–e* and **2***a–e* gave the substituted-1-arylnaphthalenes in 6 to 12% yield, along with the formation of some dimeric and polymeric products which were not further investigated.

Substituted-1-arylnaphthalenes were synthesized by an independent route and shown to be identical to the photoproducts of **1***a–e* and **2***a–e*, when compared by vapor phase chromatography (v.p.c.) (see Experimental). The syntheses of **3***a–e* and **5***a–e* were accomplished by the reaction of α-tetralone with the appropriate substituted-phenylmagnesium bromide (7). The first-formed tertiary alcohol was readily dehydrated to give 3,4-dihydro-1-arylnaphthalenes, which were not isolated. Subsequent dehydrogenation with dichlorodicyanoquinone (DDQ) gave **3***a–d* and **5***a–d*.

In order to prepare the 7-substituted-1-phenylnaphthalenes (**4***a–d*), it was necessary to synthesize 7-substituted-α-tetralones. The reaction of succinic anhydride with anisole, toluene, chlorobenzene, or fluorobenzene gave the respective 1-*p*-substitutedbenzoylpropionic acids (**8***a–d*) (8). Reduction of the acids, **8***a–d*, with zinc in hydrochloric acid (Scheme 1) gave γ-*p*-substitutedphenylbutyric acids (**9***a–d*) (9). Subsequent treatment of **9***a–d* with thionyl chloride gave the respective acid chlorides, which on cyclization with aluminum chloride yielded 7-methoxy (**10***a*) (10), 7-methyl (**10***b*) (11), 7-chloro (**10***c*) (12),

[2]



SCHEME 1

and 7-fluoro-α-tetralones (**10***d*) (13). The 7-substituted-α-tetralones, **10***a–d*, were reacted with phenylmagnesium bromide and dehydrated upon workup to give 7-substituted-3,4-dihydro-1-phenylnaphthalenes, which were not characterized but were treated with DDQ to give **4***a–d* directly.

One example of a 6-substituted-1-phenylnaphthalene, **6***a*, was prepared in a similar manner, using the commercially available 6-methoxy-α-tetralone.[3]

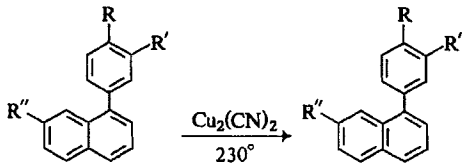
The syntheses of 1-*p*-cyanophenylnaphthalene (**3***e*), 7-cyano-1-phenylnaphthalene (**4***e*), and 1-*m*-cyanophenylnaphthalene (**5***e*) were achieved by treatment of the corresponding chloro-1-phenylnaphthalenes, **3***c*, **4***c*, and **5***c* respectively, with cuprous cyanide at 230° (14) (eq. [3]).

The substituted-1-arylnaphthalenes were characterized by their physical and spectral data (Table 3). All substituted-1-arylnaphthalenes exhibited parent ions in their mass spectra and the u.v. absorption spectra were typical of 1-phenylnaphthalene (15). The i.r. spectra were consistent with the assigned structure.

The mixtures of substituted-1-arylnaphthalenes, **3***a–e* and **4***a–e*, formed in the photocyclization of **1***a–e* were analyzed by v.p.c. (Table 4) and shown to be identical to **3***a–e* and **4***a–e* synthesized above. It can be readily seen that the photoproducts having substituents in the phenyl ring, **3***a–e*, have higher retention times than the photoproducts having substituents in the naphthalene ring, **4***a–e*, under the given v.p.c. conditions.

The mixtures of substituted-1-arylnaphthalenes **5***a–e*, **6***a–e*, and **7***a–e*, produced in the irradiation of **2***a–e*, were resolved by v.p.c. into peaks having the retention times shown in

[3]



3*c* R = *p*-Cl; R′ = R″ = H
4*c* R = R′ = H; R″ = Cl
5*c* R = R″ = H; R′ = Cl
3*e* R = *p*-CN; R′ = R″ = H
4*e* R = R′ = H; R″ = CN
5*e* R = R″ = H; R′ = CN

[3]Purchased from Aldrich Chemical Co.

TABLE 3

Physical and spectral properties of synthesized substituted-1-arylnaphthalenes[k]

Compound	Substituent	Boiling point (°C(mm))	Molecular formula	Analysis (%) Found C	Found H	Calculated C	Calculated H	Spectra: Ultraviolet λ_{max}(nm)(ε)		Mass *m/e* M^+ (% of base peak)
3*a*	*p*-Methoxy	114–115[a,b]	$C_{17}H_{14}O$	—	—	—	—	286 (11 400)	224 (59 600)	234 (100)
3*b*	*p*-Methyl	54–55[a,c]	$C_{17}H_{14}$	—	—	—	—	283 (11 500)	228 (77 100)	218 (100)
3*c*	*p*-Chloro	145–147 (0.2)[d]	$C_{16}H_{11}Cl$	—	—	—	—	284 (16 900)	221.5 (83 800)	238 (70)
3*d*	*p*-Fluoro	71–72[a,e]	$C_{16}H_{11}F$	—	—	—	—	278 (7 300)	220 (49 200)	222 (100)
3*e*	*p*-Cyano	167–171 (0.2)	$C_{17}H_{11}N$	88.70	5.07	89.02	4.84	288 (3 700)	222 (34 900)	229 (89)
4*a*	7-Methoxy	154–156 (0.1)[f]	$C_{17}H_{14}O$	87.08	5.85	87.18	5.98	289 (6 200)	232 (39 800)	234 (100)
4*b*	7-Methyl	109–111 (0.2)[g]	$C_{17}H_{14}$	—	—	—	—	288 (7 900)	228 (53 200)	218 (100)
4*c*	7-Chloro	79–80[a,h]	$C_{16}H_{11}Cl$	—	—	—	—	289 (10 600)	232 (67 200)	238 (91)
4*d*	7-Fluoro	57–59[a]	$C_{16}H_{11}F$	86.08	4.85	86.44	4.96	289 (9 600)	230 (54 400)	222 (100)
4*e*	7-Cyano	81–82[a]	$C_{17}H_{11}N$	89.47	5.11	89.02	4.84	293 (7 500)	239 (59 900)	229 (92)
5*a*	*m*-Methoxy	154–156 (0.2)	$C_{17}H_{14}O$	87.42	6.28	87.18	5.98	287 (8 400)	223 (50 700)	234 (100)
5*b*	*m*-Methyl	165–167 (2.5)[i]	$C_{17}H_{14}$	—	—	—	—	280 (6 000)	221 (37 600)	218 (100)
5*c*	*m*-Chloro	155–157 (0.2)	$C_{16}H_{11}Cl$	80.83	4.48	80.48	4.62	287 (10 000)	221 (55 600)	238 (93)
5*d*	*m*-Fluoro	130–132 (0.2)	$C_{16}H_{11}F$	86.44	5.11	86.44	4.96	285 (10 900)	224 (61 100)	222 (95)
5*e*	*m*-Cyano	161–166 (0.2)	$C_{17}H_{11}N$	88.74	4.99	89.02	4.84	281 (6 380)	219 (36 900)	229 (85)
6*a*	6-Methoxy	156–158 (0.1)[j]	$C_{17}H_{14}O$	—	—	—	—	280 (6 000)	226 (37 600)	234 (12)

[a]Melting point.
[b]Lit. (12) m.p. 116–116.5°.
[c]Lit. (23) b.p. 148–150° (0.15).
[d]Lit. (24) b.p. 151–155° (0.4).
[e]Lit. (24) m.p. 71–72°.
[f]Melting point 25°.
[g]Lit. (25) b.p. 145–150° (1.0).
[h]Lit. (12) m.p. 77–78°.
[i]Lit. (23) b.p. 140–145° (0.15).
[j]Lit. (26) b.p. 158–162° (0.1).

[k]The general structure is:

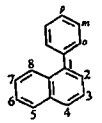


TABLE 4

The v.p.c. retention times of substituted-1-arylnaphthalenes from photocyclization of 1*a–e*

Compound	Substituent	Retention time (min)	Relative yield (%)
1*a*	*p*-MeO	9.34	—
3*a*	*p*-MeO	8.48	62
4*a*	7-MeO	7.94	38
1*b*	*p*-Me	8.67	—
3*b*	*p*-Me	7.90	41
4*b*	7-Me	7.73	59
1*c*	*p*-Cl	9.38	—
3*c*	*p*-Cl	9.22	50
4*c*	7-Cl	9.02	50
1*d*	*p*-F	7.80	—
3*d*	*p*-F	6.98	92
4*d*	7-F	7.12	8
1*e*	*p*-CN	10.10	—
3*e*	*p*-CN	9.40	33
4*e*	7-CN	9.22	67

TABLE 5

The v.p.c. retention times of substituted-1-arylnaphthalenes from photocyclization of 2*a–e*

Compound	Substituent	Retention time (min)	Relative yield (%)
2*a*	*m*-MeO	9.68	—
5*a*	*m*-MeO	8.60	55
6*a*	6-MeO	8.72	33
7*a*	8-MeO	8.00	12
2*b*	*m*-Me	9.32	—
5*b*	*m*-Me	8.00	52
6*b*	6-Me	8.10	38
7*b*	8-Me	7.22	10
2*c*	*m*-Cl	9.82	—
5*c*	*m*-Cl	8.86	62
6*c*	6-Cl	8.66	25
7*c*	8-Cl	8.22	13
2*d*	*m*-F	8.08	—
5*d*	*m*-F	6.82	87
6*d*	6-F	6.25	7.5
7*d*	8-F	6.20	5.5
2*e*	*m*-CN	10.04	—
5*e*	*m*-CN	8.82	52
6*e*	6-CN	8.75	42
7*e*	8-CN	7.72	6

Table 5. Compounds, 5*a–e*, synthesized above were shown to have identical retention times to one of the long retention time peaks. Compound 6*a* was shown to be identical to the other long retention time peak observed in the v.p.c. of the photoproducts of 2*a*. The short retention time peaks were thus assigned to 7*a–e* (see below).

TABLE 6

Assignment of methoxy and methyl protons in the n.m.r. spectra of substituted-1-arylnaphthalenes

Compound	Substituent	Peak (p.p.m.)
1*a*	*p*-MeO	3.83
3*a*	*p*-MeO	3.78
4*a*	7-MeO	3.65
1*b*	*p*-Me	2.12
3*b*	*p*-Me	2.15
4*b*	7-Me	2.42
2*a*	*m*-MeO	3.80
5*a*	*m*-MeO	3.72
6*a*	6-MeO	3.64
7*a*	8-MeO	3.27
2*b*	*m*-Me	2.36
5*b*	*m*-Me	2.25
6*b*	6-Me	2.32
7*b*	8-Me	1.85

The relative yields of the substituted-1-arylnaphthalenes 5*a–e*, 6*a–e*, and 7*a–e*, were determined by measurement of the areas under the peaks in the v.p.c. The assignments of the peaks having the shortest retention times to 7*a–e* are consistent with the fact that 7*a–e* are produced in the lowest yield. Photocyclization of 2*a–e* ortho to the substituent of the phenyl ring giving 7*a–e* would be sterically unfavorable compared to photocyclization of 2*a–e* para to the substituent of the phenyl ring giving 6*a–e*.[4]

The nuclear magnetic resonance (n.m.r.) spectra of the mixture of substituted-1-arylnaphthalenes produced by the irradiation of 2*a* and 2*b* was extremely informative and aided us in affirming the assignment of 6*a*, 7*a* and 6*b*, 7*b*. From Table 6 it is seen that the n.m.r. spectrum of the mixture of 5*a*, 6*a*, and 7*a* obtained in the photocyclization of 2*a* gives us three absorption peaks representing the methoxy protons of 5*a*, 6*a*, and 7*a*. Two of these peaks have been absolutely assigned to 5*a* and 6*a* by comparison with the pure synthesized products. The third absorption peak at 3.27 p.p.m. has been assigned to the methoxy protons of 7*a*, which thus exhibit an upfield shift of 0.4 p.p.m. relative to the methoxy protons of 6*a*. This upfield shift of the methoxy protons of 7*a* is expected, due to the shielding effect of the phenyl group at the

[4]The yields of 6*d* and 7*d* are very close and hence a firm assignment based on product yield is not possible. The retention times of 6*d* and 7*d* are very similar and thus the given assignments to these peaks are only tentative.

1-position of **7***a* (16) and substantiates the assignment of the peak at 3.27 p.p.m. to the methoxy protons of **7***a*. Similarly, the absorption peak at 1.85 p.p.m. exhibited in the n.m.r. spectrum of the mixture of **5***b*, **6***b*, and **7***b* obtained from the photocyclization of **2***b* substantiates the presence of **7***b*.

Thus n.m.r., v.p.c., and product yield data strongly indicate the formation of **7***a–e* in the photocyclization reactions of **2***a–e*.

The product distribution data of Table 4, showing the relative yields of **3***a–e* and **4***a–e* from the photocyclization of **1***a–e* and the data from Table 5 showing the relative yields of **5***a–e*, **6***a–e*, and **7***a–e* from the photocyclization of **2***a–e* clearly show that a substituent on a phenyl ring of 1,4-diphenyl-1,3-butadiene does not appreciably influence the direction of photocyclization. The major exception to this finding is the photocyclization of **1***d* and **2***d* which gives mainly photoproducts **3***d* and **5***d*. The fluoro substituents cause cyclization to occur to the unsubstituted phenyl ring. The photocyclization of **1***e* gives a slight preponderance of **4***e* over **3***e* (2:1).

The possibility that some of the substituted-1-arylnaphthalenes were undergoing photo-decomposition could not be overlooked in evaluating the relative yields of the photoproducts. All substituted-1-arylnaphthalenes were irradiated under conditions identical to those for **1***a–e* and **2***a–e* and found to be unchanged even after 6 days irradiation.

Thus selective photo-decomposition of the minor photo-products **4***d*, **6***d*, and **7***d* in the photocyclization reactions **1***d* and **2***d* cannot be the reason for the high relative yield of **3***d* and **5***d* and the correct explanation must await further studies.

Although a detailed mechanistic study of the parent 1,4-diphenyl-1,3-butadiene has not yet been undertaken, the closely related fulgicides have been shown to proceed through a 1,2-dihydronaphthalene intermediate which on dehydrogenation gives a 1-phenylnaphthalene type compound (17). In all probability the mechanism of photocyclization of **1***a–e* and **2***a–e* proceeds through similar intermediates. Further studies on the detailed mechanism of the photocyclization of 1-substitutedphenyl-4-phenyl-1,3-butadienes and related diaryl polyenes are currently in progress.

Experimental

All melting points were determined on a Kofler hot stage and are corrected. The i.r. spectra were recorded on a Perkin–Elmer 257 i.r. spectrophotometer using KBr discs. The u.v. spectra were measured using a Cary 14 u.v. spectrometer and 95% ethanol as solvent. The n.m.r. spectra were measured on a Varian A60 spectrometer using tetramethylsilane as an internal standard ($\delta = 0$ p.p.m.) and deuterochloroform as solvent. Mass spectra were recorded on a Hitachi–Perkin–Elmer RMU-6D mass spectrometer. Column chromatography was performed using Woelm alumina, activity II–III; silica gel was used for thin- and thick-layer chromatography. All photochemical reactions were carried out in a Rayonet photochemical reactor using RPR 3500 Å lamps. Microanalyses were performed by Dr. C. Daesslé of Montreal.

Vapor Phase Chromatography

Vapor phase chromatographic measurements were made under standard conditions. A Hewlett–Packard 700 gas chromatograph equipped with a 6 ft stainless steel column packed with silicone rubber SE-30 810 was used for product analysis. The column temperature was programmed at 30 °C per min from 70 to 250 °C and then maintained at the upper limit until all compounds had been eluted. Flow rate was kept constant at 40 ml per min of helium. The detector and injection port temperatures were maintained at 275 °C. All analyses were run in diethyl ether solution and retention times are measured with reference to the ether peak.

Synthesis of 1-Monosubstitutedphenyl-4-phenyl-1,3-butadienes

Method A

A typical example is given for the preparation of 1-*m*-methoxyphenyl-4-phenyl-1,3-butadiene. To a mixture of 11.5 g of (0.025 moles) triphenylcinnamylphosphonium bromide and 3.5 g (0.026 moles) of *m*-methoxybenzaldehyde in 100 ml methanol, was added 130 ml of 0.2 *M* lithium methoxide. The mixture was allowed to crystallize overnight after which crystals of 1-*m*-methoxyphenyl 4-phenyl-1,3-butadiene were filtered off.

Method B

The remaining 1-substitutedphenyl-4-phenyl-1,3-butadienes were prepared by reacting a monosubstituted-benzylphosphonium bromide and cinnamaldehyde by a procedure identical to method A (Table 1).

Preparation of Benzyltriphenylphosphonium Bromides

All substitutedbenzyltriphenylphosphonium bromides were synthesized in a manner identical to that of *p*-methylbenzyltriphenylphosphonium bromide described previously (6). A mixture of 25.0 g (0.135 moles) of 4-bromo-*p*-xylene and 44 g (0.17 moles) of triphenylphosphine in 160 ml dimethyl formamide was refluxed overnight. After cooling to room temperature, the salt crystallized out of the solution and was filtered. The physical data for the phosphonium salts used in method B is described in Table 7.

Irradiation of 1-Substitutedphenyl-4-phenyl-1,3-butadienes

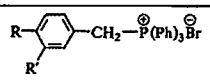
The photochemical experiments were carried out at concentrations of 1×10^{-3} *M* in 1,3-butadiene and 2×10^{-3} *M* iodine in 500 ml of dry benzene under a

TABLE 7

Substitutedbenzyltriphenylphosphonium bromides*

Substituents	Melting point (°C)	Yield (%)	Analysis (%) Found C	Found H	Calculated C	Calculated H
R′ = H, R = CN	~350		68.42	4.75	68.26	4.59
R′ = CN, R = H	~350†		68.38	4.53	68.26	4.59
R′ = H, R = Me	293–295‡		—	—	—	—
R′ = Me, R = H	267–269§		—	—	—	—

*The compound has the following general structure:



†Lit. (21) m.p. 311–320°.
‡Lit. (6) m.p. 276–277°.
§Lit. (27) m.p. 271–272°.

nitrogen atmosphere. For irradiation of 1-methoxyphenyl-4-phenyl-1,3-butadienes concentrations of 5×10^{-4} *M* were used to minimize polymer formation. The reactions were followed by u.v. spectroscopy, aliquots being taken from the reaction vessel at selected times. The characteristic absorption peaks of the 1-substitutedphenyl-4-phenyl-1,3-butadienes gradually disappeared over 3 days (6 days when the substituents were cyano group) and $\lambda_{max} = 220$ mμ characteristic of phenylnaphthalenes appeared.

After the photochemical reaction was complete the benzene solution was washed with aqueous sodium thiosulfate and dried over anhydrous magnesium sulfate. The benzene solution was concentrated and passed through an aluminum column (20 g) to remove polymers. The phenylnaphthalenes were isolated by preparative thick-layer chromatography (t.l.c.) using hexane as eluant. All phenylnaphthalenes moved faster than the starting 1,3-butadienes on t.l.c. Compounds moving slower than the starting material invariably turned out to be dimeric products as shown by mass spectroscopy. The mixtures of phenylnaphthalenes obtained in this manner were analyzed by v.p.c. to give two substituted-1-arylnaphthalenes in the case of the photocyclization of 1-*p*-substitutedphenyl-4-phenyl-1,3-butadiene (**1***a–e*) and three substituted 1-arylnaphthalenes for the photo products of 1-*m*-substitutedphenyl-4-phenyl-1,3-butadienes (**2***a–e*).

The total yields of phenylnaphthalenes varied from 6–12%.

Preparation of Substituted-α-tetralones

The substituted-α-tetralones were prepared essentially as described in reference 13. A typical synthesis of an α-tetralone is represented by the following synthesis of 7-fluoro-α-tetralone. A mixture of 16.0 g of *p*-fluorophenylbutyric acid (18) and 10 ml (0.13 moles) of redistilled thionyl chloride under dry nitrogen was warmed until the acid melted. The reaction proceeded for 30 min without further heating. The mixture was then heated for 10 min on a steam bath. The excess thionyl chloride was removed by distillation under reduced pressure from a water pump. To the flask, cooled in an ice bath and fitted with a reflux condenser was added 80 ml of carbon disulfide and 15 g (0.115 moles) of anhydrous aluminum chloride. After the rapid evolution of hydrogen chloride had ceased, the mixture was slowly warmed to the boiling point. After heating and shaking for 10 min the reaction was complete. The reaction mixture was cooled to 0 °C and the aluminum chloride complex was decomposed by careful addition of 50 g of ice. To this mixture was now added 12 ml of concentrated hydrochloric acid. The mixture was then separated and extracted with ether. The combined ether – carbon disulfide layer was separated, dried over magnesium sulfate, and vacuum distilled to give 7-fluoro-α-tetralone (**10***d*) b.p. 93–96° (1.4 mm). On cooling the oil crystallized to give **10***d*, m.p. 66–68° in 69% yield.

Anal. Calcd. for $C_{10}H_9FO$: C, 73.18; H, 5.49. Found: C, 73.15; H, 5.55.

Synthesis of Substituted-1-arylnaphthalenes

Substituted-1-arylnaphthalenes were prepared by reaction of a suitably substitutedphenyl Grignard to a suitable α-tetralone as previously described (7, 12) to give a substituted-3,4-dihydro-1-arylnaphthalene. The dihydro compound was dehydrogenated with an equivalent amount of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in refluxing benzene for 15 h. The resulting substituted-1-arylnaphthalene was purified by t.l.c. The cyano substituted phenylnaphthalenes were not prepared by this method.

Preparation of Cyano Substituted Phenylnaphthalenes

A typical procedure is given for the synthesis of 1-*p*-cyanophenylnaphthalene. A mixture of 0.3 g (0.0012 moles) of 1-*p*-chlorophenylnaphthalene and 0.25 g (0.028 moles) of cuprous cyanide was refluxed for 24 h at 230 °C with the exclusion of moisture. The reaction product was purified on preparative t.l.c. on elution with hexane:benzene (1:1) to give 1-*p*-cyanophenylnaphthalene, b.p. 167–171° (0.2 mm) in 58% yield.

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