

The Wavelength- and Solvent-dependent Photochemistry of 1,1-Dicyano-2-methyl-4-phenylbut-1-ene; Reaction from Two Excited States¹

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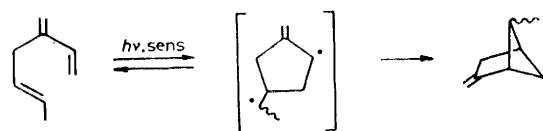
1,1-Dicyano-2-methyl-4-phenylbut-1-ene (4), on u.v. irradiation in solution, yields two products, 3,3-dicyano-2-methyl-4-phenylbut-1-ene (5) and 1-dicyanomethyl-1-methylindane (6). The photoreaction is dependent both on solvent polarity and on the excitation wavelength. A long-wavelength band in the absorption spectrum of (4), not present in the spectra of its isolated chromophores, is attributed to an intramolecular charge-transfer interaction. The unusual dependence on solvent and wavelength is explained in terms of a reaction mechanism in which (5) is formed from a delocalised excited state, with a staggered conformation, and (6) from a charge-transfer excited state, with an eclipsed conformation.

THE extensive study made in recent years of the di- π -methane rearrangement,² which is exhibited by compounds containing a 1,4-diene unit, has renewed our interest in the comparatively neglected photochemistry of 1,5-diene systems.^{3,4} The photochemistry of 1,5-dienes, which have been termed 'di- π -ethane' systems,⁵ is of interest because of the possibility of bonding interactions between the π -bonds leading to product formation.

Limited studies of the photochemistry of 1,5-dienes have already been carried out, the reaction common to nearly all these compounds being the formation of bicyclo[2.1.1]hexanes *via* an initial 1,5-bonding interaction between the π -bonds.⁶ This is illustrated in Scheme 1 for the case of 3-methylenehepta-1,5-diene.⁷

This preference for 1,5-, as opposed to 1,4- or 1,6-bonding, is shown in almost every case,^{8,9} even when the 'diradical' thus formed is not, *a priori*, the most stable.^{7,8} No satisfactory explanation has been advanced for the ubiquitous nature of this preference,[‡] which is also seen in ground-state radical cyclisation.^{10,11}

Of the more complex di- π -ethane systems studied, which include arylalkenes,¹² aryldienes,¹³ and 1,2-diarylethanes,⁵ only the photoreaction of 4-phenylbut-1-ene (1) can be directly compared to those of the simple



SCHEME 1

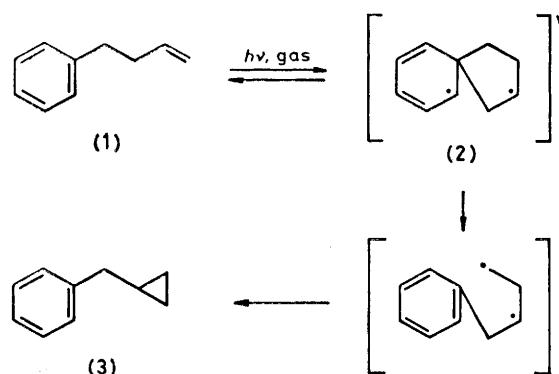
1,5-dienes. Gas-phase, unsensitized photolysis gave benzylcyclopropane (3) as the major product.³ Reaction was postulated to occur *via* a vibrationally excited intermediate (2) resulting from an initial 1,5-bonding interaction.

Arylalkenes have an inherent advantage over non-aromatic dienes in that they fluoresce. Measurement of fluorescence parameters can give quantitative inform-

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‡ Liu and Hammond⁷ and Kaupp,⁶ consider this effect to have geometrical origins. Salisbury³ discusses the possibility of control by orbital symmetry.

ation about competing excited-state processes. Thus we chose the 4-phenylbut-1-ene skeleton for further studies of the photochemistry of di- π -ethane systems in solution.



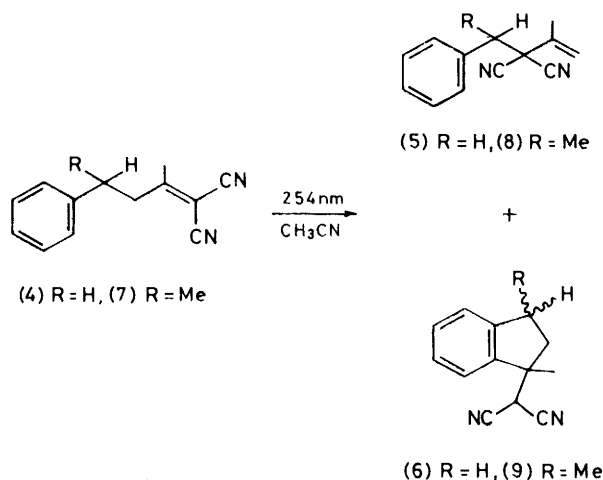
4-Phenylbut-1-ene itself does not react in solution,³ presumably because vibrational excitation is necessary to overcome the large activation barrier expected for disruption of the aromatic ring.¹⁴ It was anticipated, however, that substitution of the olefinic double bond with cyano-groups would lead to a lowering of this activation barrier, through the ability of these substituents to stabilise intermediates of type (2).¹⁵ We present here the results of a study of the photochemistry of 1,1-dicyano-2-methyl-4-phenylbut-1-ene (4) in solution. §

RESULTS AND DISCUSSION

On irradiation in acetonitrile at 254 nm, (4) reacted to form (5) and (6) (Scheme 2). 3,3-Dicyano-2-methyl-4-phenylbut-1-ene (5) results from a 1,3-benzyl shift, a reaction that has already been observed for the closely related compound 1,1-dicyano-2-methyl-4-phenylpent-1-ene (7).¹⁶ The reaction leading to formation of 1-dicyanomethyl-1-methylindane (6), however, has not been previously observed. The structure of (6) was verified by the synthesis shown in Scheme 3.

§ (*E*)- and (*Z*)-1-Cyano-2-methyl-4-phenylbut-1-ene and 2-cyano-3-methyl-4-phenylbut-1-ene have also been studied. They undergo an interesting photoreaction, different to that observed for (4), which is currently the subject of further investigation.

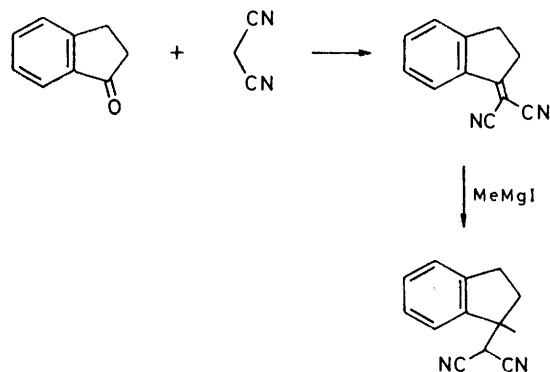
Formation of (6) on irradiation of (4) can be rationalised in terms of an initial, 1,5-bonding interaction followed by a hydrogen-shift (Scheme 4). The presence of the cyano-substituents leads to an initial bonding interaction dif-



SCHEME 2

ferent from that observed in the case of 4-phenylbut-1-ene (1).

Dependence of the Photoreaction of (4) on Solvent Polarity.—A marked dependence on solvent polarity was observed for the photoreaction of (4) (Table 1). A comparison of the quantum yields for formation of (5) and (6) in acetonitrile and cyclohexane [λ_{ex} 275 nm, acetonitrile: $\Phi(5)$ 0.0055, $\Phi(6)$ 0.018; cyclohexane: $\Phi(5)$ 0.034, $\Phi(6) \leq 1 \times 10^{-4}$] suggests that the reaction of (4) to give (6) is responsible for this solvent dependence,



SCHEME 3

formation of (5) being relatively unaffected. This implies that charge-separation occurs on the pathway leading from excited (4) to ground-state (6). This can most readily be accommodated by postulating that the 'intermediate' formed upon 1,5-bonding is best described as a resonance mixture of a diradical (10) and a zwitterionic species (11) (Scheme 4). Formation of such a dipolar 'intermediate' would be favoured by a solvent of high polarity.

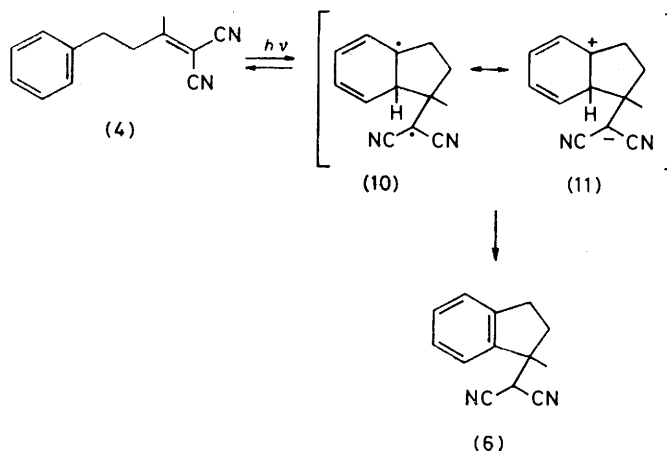
TABLE 1

Ratios of product formation on irradiation ($\lambda_{\text{ex}} > 270$ nm) of (4) in different solvents

Solvent	C_6H_{12}	Et_2O	CH_2Cl_2	CH_3CN
ϵ^a	2.0	4.3	8.9	37.5
Ratio (6) : (5)	0.0	0.1	0.2	2.9

^a Dielectric constant.

It is of interest to note that involvement of a similar charge-separated species has been postulated in the di- π -methane rearrangement of 1,1-dicyano-2-methyl-3-phenylprop-1-ene.^{15c} In that case, however, the charge-separated species was proposed to lie on a deactivating pathway competing with the di- π -methane rearrangement.

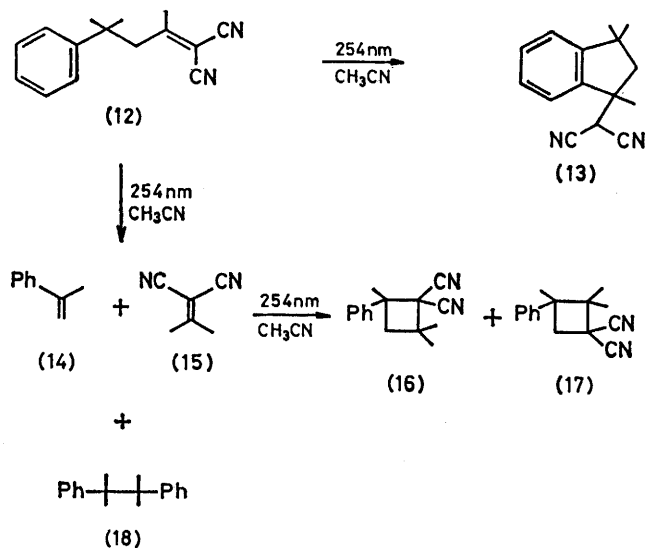


SCHEME 4

The Effect of Benzylic Alkyl Substitution.—The dependence on solvent polarity also explains why formation of the indane (9) was not observed on irradiation of (7) in non-polar solvents.¹⁶ We have investigated the photoreactions of both 1,1-dicyano-2-methyl-4-phenylprop-1-ene (7) (Scheme 2) and 1,1-dicyano-2,4-dimethyl-4-phenylpent-1-ene (12) (Scheme 5) in acetonitrile. An indane product analogous to (6) was formed in both cases. However, no evidence was obtained for the occurrence of a reaction of the type shown in Scheme 6. By analogy with the di- π -methane rearrangement one might expect this alternative reaction pathway to be favoured when the carbon bearing the radical centre formed on cleavage has alkyl substituents.¹⁷ A direct comparison, however, is not possible since in Scheme 6 a hydrogen-shift is necessary, in addition to cleavage, in order to regenerate the aromatic ring. In the related step in the di- π -methane rearrangement only cleavage is required.²

Dependence of the Photoreaction of (4) on Wavelength.—In addition to its dependence on solvent polarity the photoreaction of (4) displays a pronounced dependence on wavelength, as can be seen from the quantum yields for formation of (5) and (6) in acetonitrile and of (5) in cyclohexane (Table 2).

For a reaction dependent on wavelength it is obviously of interest to consider the u.v. absorption spectrum of the



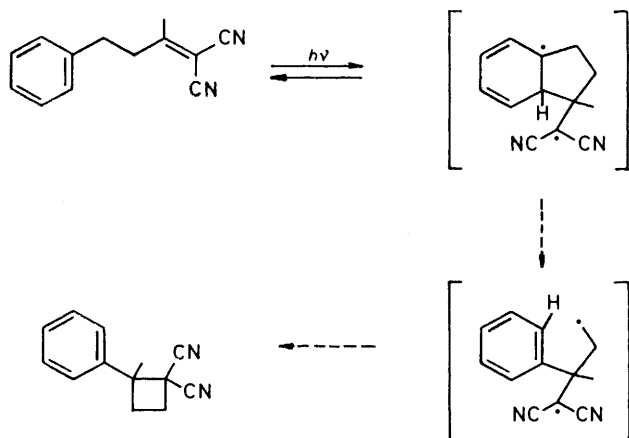
SCHEME 5

TABLE 2

Product ratios and quantum yields of product formation on irradiation of (4) at different wavelengths

Solvent	$\lambda_{\text{ex}}/\text{nm}^a$	Φ (5)	Φ (6)	Product ratio (6) : (5)
CH ₃ CN	225	<i>b</i>	<i>b</i>	0.44
CH ₃ CN	230	0.015 ^c	0.0065 ^c	0.43
CH ₃ CN	250	0.015 ^d	0.008 ^d	0.53
CH ₃ CN	275	0.0055 ^d	0.018 ^d	3.3
CH ₃ CN	290	0.0016 ^e	0.013 ^e	8.1
CH ₃ CN	300	$< 1 \times 10^{-4}$ ^e	0.008 ^e	> 80
C ₆ H ₁₂	250	0.062 ^d	$< 1 \times 10^{-4}$ ^e	
C ₆ H ₁₂	275	0.034 ^d	$< 1 \times 10^{-4}$ ^e	

^a Bandpass 19 nm. ^b Lamp intensity too low to allow determination of quantum yields. ^c $\pm 20\%$. ^d $\pm 10\%$. ^e No product detected.



SCHEME 6

reactant. That of (4) (Figure 1) is seen to contain a large, long-wavelength band which is not present in the spectra of either of its component chromophores, toluene and 1,1-dicyano-2-methylpropene (DCMP). The absorption spectrum obeyed Beer's law over a wide concentration range and the new band must thus arise from

an intramolecular interaction (or interactions) between the two chromophores in (4).

Substituent effects suggest that this interaction is of a charge-transfer (c.t.) nature. The *para*-cyano- and *para*-methoxy-substituted compounds (19) and (20)*

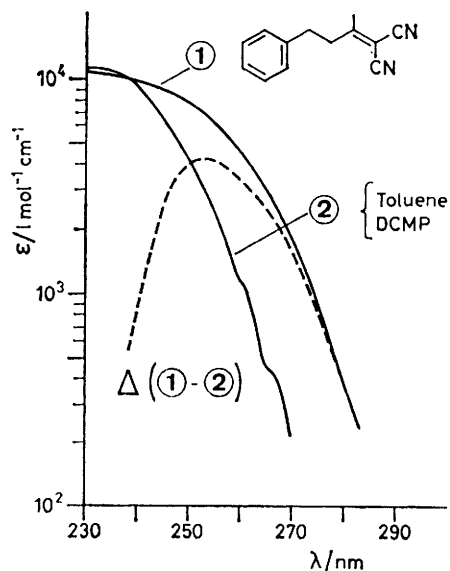
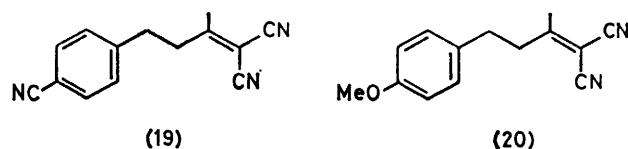


FIGURE 1 U.v. difference spectrum for (4) in acetonitrile (---) derived from the u.v. spectrum of (4) and the sum of the u.v. spectra of its component chromophores

both have similar long-wavelength bands in their u.v. spectra. The correlation between the maxima of the long-wavelength bands in (4), (19), and (20) with the



variation in ionisation potential (I_p) of the aryl group (Table 3) is in accord with a c.t. interaction between the aryl group (donor) and the DCMP group (acceptor).

TABLE 3

Variation of λ_{max} (c.t.) with I_p (aryl group) for (4), (19), and (20) in acetonitrile

Compound	(19)	(4)	(20)
λ_{max} (c.t.)/nm	245	255	260
I_p (aryl group)/eV	9.76 ^a	8.82 ^b	8.05 ^c

^a I_p *p*-toluonitrile. ^b I_p toluene. ^c I_p *p*-methylanisole; *a* and *b* from 'Handbook of Chemistry and Physics', ed. R. C. Weast, CRC Press, 1979—1980, 60th edn., p. E-75; *c* measured on a Perkin-Elmer PS 18 by Mr. W. Sonntag, Institut für Strahlenchemie, Mülheim.

Further evidence for a state resulting from intramolecular charge-transfer comes from the fluorescence

* The synthesis and photochemistry of (19) and (20) will be the subject of a future publication.

emission of (20).† A broad, structureless emission was observed between 300 and 600 nm (Figure 2). This long-wavelength emission showed a large bathochromic shift upon increasing solvent polarity and must thus occur from a highly polar excited state such as that

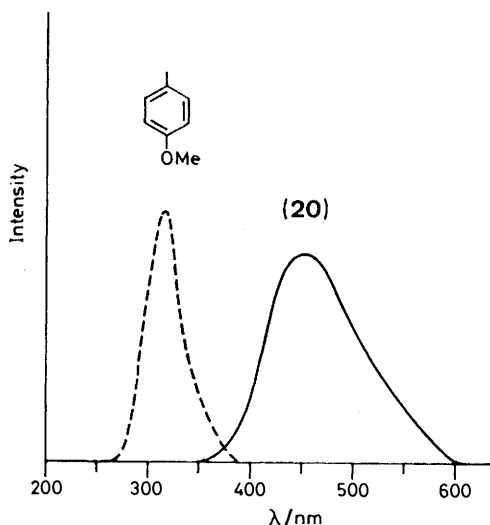


FIGURE 2 Fluorescence emission spectra of (20) and *p*-methylanisole in methylene chloride; not to scale

which would be formed by intramolecular electron transfer between the two chromophores in (20).¹⁸ No emission from the singlet excited aryl group was observed and the DCMP group is not expected to fluoresce.

Two interactions of a c.t. nature can be envisaged for (4). An interaction through space, involving direct orbital overlap between the chromophores, and an interaction through the intervening bonds, in which the chromophores couple by overlap of the π -orbitals with the σ -orbitals of the C-C chain.¹⁹

A through-space interaction in (4) requires the adoption of an eclipsed conformation (Figure 3). Orbital

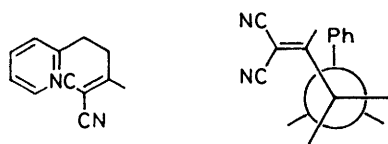


FIGURE 3

overlap could then result in a transition to a c.t. excited state with the same conformation. A new band would appear in the absorption spectrum.²⁰

The possibility of a through-bond interaction between two chromophores was first considered for the case of a 1,5-diene.²¹ If the diene is in a conformation such that the central 3,4-single bond is in a plane at right angles to both double bonds then the π -systems will be coupled by

† No fluorescence emission was observed from degassed solutions of (4) and (19) in acetonitrile or cyclohexane, implying $\Phi_f \leq 1 \times 10^{-3}$.

overlap with the central σ -bond, splitting both the π and π^* levels (Figure 4). As a result there will be two low-energy electronic transitions, one in much the same region as the original transition and one to longer wavelength. For an unsymmetrical system, *i.e.* one containing an electron donor and an electron acceptor, the excited state populated by these transitions should have a degree of c.t. character.

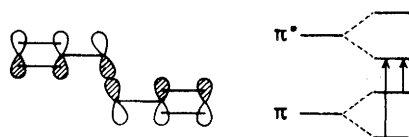
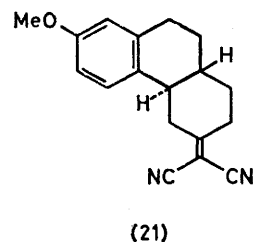


FIGURE 4

Since then, many examples have been published of through-bond c.t. interactions.²² Of particular interest is the recent work by Pasman *et al.* on (20) and its conformationally inflexible analogue (21).¹⁸ Both had virtually identical fluorescence spectra and, since (21) cannot adopt an eclipsed conformation, the c.t. excited state was postulated to arise through a through-bond interaction between the chromophores. We note that



(21)

the thermodynamically most stable ground state conformer of (4) is suitably oriented for a similar through-bond interaction (Figure 5).

Postulated Mechanism for the Photoreaction of (4).—The photoreaction of (4) can be rationalised if it is assumed that both a through-space and a through-bond

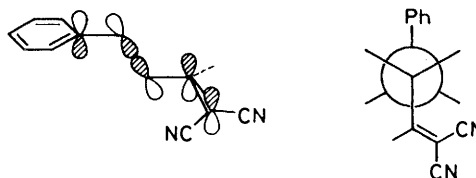


FIGURE 5

interaction occur. It follows from this assumption that there will be two low-lying excited states, a delocalised state, with an open conformation (Figure 5), resulting from a through-bond interaction, and a c.t. state, with a folded conformation (Figure 3), resulting from a through-space interaction. The two excited states will be

associated with three u.v. absorption bands (Figure 6).^{*} Excitation in either of the through-bond bands will populate the open excited state while excitation in the through-space band will populate the folded, c.t. excited state.

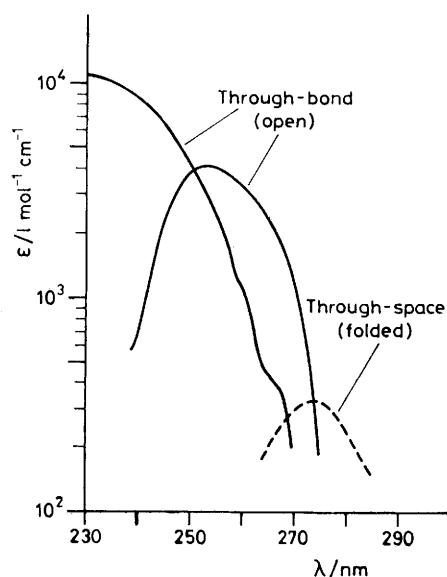


FIGURE 6 Postulated arrangement of the u.v. absorption bands corresponding to the through-bond (open) and through-space (folded) excited states in (4)

Interconversion between the two states will require a gross conformational change and should thus be slow ($k \approx 1 \times 10^8$ – 1×10^9 s⁻¹ from kinetic studies of other intramolecular systems²⁴). This in turn implies that reaction could compete with this interconversion. The dependence on wavelength of the photoreaction of (4) can be explained if (5) is formed from one excited state and (6) from the other.²⁵ We propose that (6) is formed from the folded, c.t. state (the folded conformation bringing the bonding carbon atoms close together and the polar character of this state explaining the observed dependence on solvent polarity) and (5) from the open, delocalised state † (Figure 7).

Thus in acetonitrile at 275 nm the majority of the incident light is absorbed by the folded conformer (Figure 6), formation of (6) is favoured and the product ratio, (6) : (5) = 3.3 (Table 2). At longer wavelengths the proportion of light absorbed by the folded conformer

* The arrangement of the bands in Figure 6, which is used to illustrate the proposed mechanism and provides no evidence for it, was derived from the u.v. spectrum of (4) in acetonitrile. The through-space, c.t. band, expected to be most affected by changes in solvent polarity, was obtained by subtracting the spectrum of (4) in cyclohexane from that in acetonitrile. The remainder was divided into two through-bond bands by assuming one of them to be identical to the hypothetical absorption of (4) in the absence of any interaction, *i.e.*, the sum of the spectra of the component chromophores (Figure 1). With respect to the postulated reaction mechanism only the position of the through-space band relative to the through-bond bands is of importance and we note that there is tentative evidence in the case of another D-(CH₂)₂-A system that the through-space band lies to the red of the through-bond bands.²³

increases still further, hence at 290 nm, (6) : (5) = 8.1 and at 300 nm, (6) : (5) > 80. At 250 nm, however, the open conformer absorbs most of the light and (6) : (5) = 0.53. At still shorter wavelengths the quantum yields change very little and the product ratio, (6) : (5) does not fall to zero but rather reaches a constant value. Thus at 230 nm (6) : (5) = 0.44 and at 225 nm, (6) : (5) = 0.43. From this it can be concluded that reaction from the open, delocalised excited state to form (5) competes with interconversion to the folded, c.t. state. Such an interconversion is equivalent to intramolecular exciplex formation²⁶ and implies that (in acetonitrile) the open, delocalised state is equal to, or higher in energy than, the folded, c.t. state. The observation that the reaction is only dependent on wavelength on excitation at wavelengths >250 nm is important since it requires the

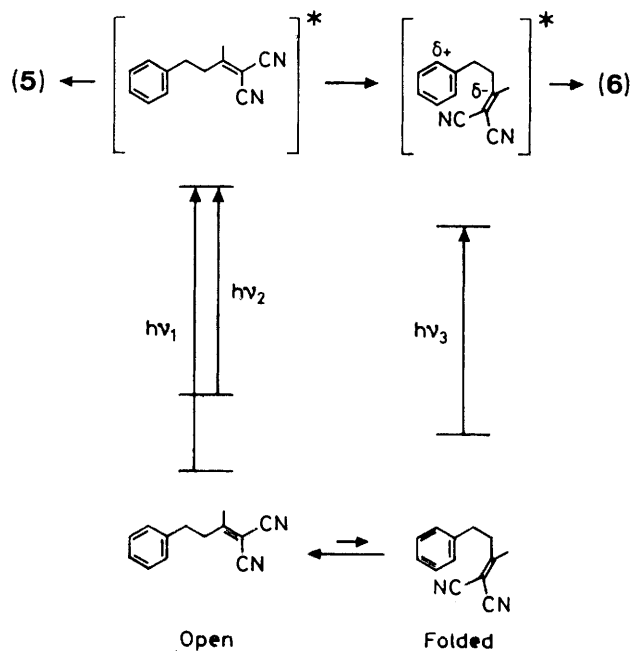


FIGURE 7

division of the long-wavelength band of (4) (Figure 1) into more than one component.

The proposed mechanism also explains the wavelength-dependence of the reaction in cyclohexane (Table 2). In cyclohexane, however, absorption by the folded state, while causing a decrease in $\Phi(5)$, does not lead to formation of (6). This is presumably due to lack of stabilisation of the highly polar 1,5-bonded 'intermediate' [(10) \leftrightarrow (11)] by the non-polar solvent. In

† Theoretical considerations suggest that a through-bond interaction will weaken the central 3,4-bond and thus favour a 1,3-benzyl shift.^{19c}

‡ For the sake of simplicity only two conformations of (4) are discussed above while, in fact, an infinite number of different conformers exist. The observed absorption spectrum of (4) will be a composite of all the different absorption spectra and two families of excited states will exist, based on the open, delocalised and folded, c.t. states, with the states corresponding to the conformers discussed above being of lowest energy.

addition, the energy of the folded, c.t. state should be raised relative to that of the open, delocalised state.* This might explain the increase in $\Phi(5)$ on going from acetonitrile to cyclohexane.

EXPERIMENTAL

Instrumentation.—G.l.c. was performed on a Pye-105 gas chromatograph using packed 1/4- or 1/8-in glass columns with nitrogen as the carrier gas. Unless otherwise stated the liquid coating used was OV17. Preparative g.l.c. was performed on a Pye-104 gas chromatograph with 3/8-in glass columns and an all glass 100 : 1 splitter. Mass spectra were obtained, at 15 or 70 eV, on an A.E.I.-M.S. 12 instrument fitted with a Digispec P.D.P.-8 data system. G.l.c.-m.s. were obtained on the M.S. 12 which was coupled to a Pye-104 gas chromatograph (helium carrier gas) *via* a silicone rubber membrane separator. N.m.r. spectra were obtained either on a Perkin-Elmer R12 (60 MHz, continuous wave) or on a Varian XL-100 (100 MHz, continuous wave or Fourier-transform) instrument. The spectra, run in CDCl_3 unless otherwise stated, are presented as chemical shifts on the δ scale relative to tetramethylsilane. U.v. spectra were obtained on a Unicam SP-1800 spectrophotometer and i.r. spectra on a Perkin-Elmer 157-G spectrophotometer. M.p.s were measured on a Gallenkamp melting point apparatus and are uncorrected. Bulb-to-bulb distillations were performed on a Kugelrohr apparatus with an electrically heated oven. Elemental analyses were performed by the Microanalysis Service of University College, London, and Dornis and Kolbe, Mulheim a. d. Ruhr, West Germany. Fluorescence spectra were measured on a spectrofluorimeter consisting of a 450-W high-pressure Xenon lamp (Wotan XB0450W), quartz condensing lenses, a Bausch and Lomb high-intensity excitation monochromator (0.75-mm exit slit, 5-nm bandpass), a cell holder, a photodiode (RCA 935), a Hilger and Watts motor driven emission monochromator (D330), and a photomultiplier (RCA IP28) whose amplified signal was fed to a chart recorder.

Synthesis of Starting Materials.—1,1-Dicyano-2-methyl-4-phenylbut-1-ene (4) and its derivatives (7), (12), (19), and (20) were synthesised by the Knoevenagel condensation of malononitrile with the corresponding ketones.²⁷

Synthesis of 1,1-Dicyano-2-methyl-4-phenylbut-1-ene²⁸ (4).—Benzylacetone (16.3 g, 0.11 mol), malononitrile (7.35 g, 0.11 mol), and glacial acetic acid (6.8 g, 0.11 mol) were dissolved in dry benzene (200 ml). Ammonium acetate (1.94 g, 0.03 mol) was added and the mixture refluxed for 10 h (Dean and Stark head; water condenser).† The solution was washed (NaHCO_3 ; water), dried (MgSO_4), concentrated, and fractionally distilled: fraction 2 (140–160°; 0.3 Torr) was 1,1-dicyano-2-methyl-4-phenylbut-1-ene (83%, 18 g, 0.092 mol). Since this compound tends to break down on distillation it was further purified by vacuum sublimation (100°; 1 Torr) and recrystallisation (ethanol-cyclohexane) to yield a crystalline solid; m.p. 43–44 °C, *m/e* 91 (100%), 92 (7.8), 65 (7.6), 196 (4.7, M^+), 39 (3.1), 51 (2.6), 63 (1.6),

and 77 (1.5); δ (100 MHz) 7.3 (5 H, s, Ph), 2.85 (4 H, s, coincident CH_2 's), 2.2 (3 H, s, CH_3); Eu(fod)₃ split the singlet at δ 2.85 giving the expected A_2B_2 splitting pattern; ν_{max} (Nujol) 2240 cm⁻¹ (CN str.) and 1650 w cm⁻¹ (C=C); λ_{max} (C_6H_{12}) 231 nm (ϵ 11 200), λ_{max} (CH_3CN) 232 nm (ϵ 10 900); u.v. spectra of (4) in acetonitrile determined at 7.93×10^{-2} , 10^{-3} , 10^{-4} , and 10^{-5}M in 0.001, 0.01, 0.1, and 1.0 cm cells were identical (Found: C, 79.55; H, 6.2; N, 14.35. Calc. for $\text{C}_{13}\text{H}_{12}\text{N}_2$: C, 79.55; H, 6.15; N, 14.25%).

Synthesis of 1,1-Dicyano-2-methyl-4-phenylpent-1-ene (7).—(a) **1-Bromo-1-phenylethane.** Ethylbenzene (54.0 g, 0.51 mol) in a solution of bromine in methylene chloride (500 ml, 0.776M in Br_2) was refluxed for 1.5 h with illumination from a sun-ray lamp. The solution was washed (NaHCO_3 ; water), dried (Na_2SO_4), concentrated, and fractionally distilled: fraction 2 (88–91 °C, 14 Torr) was 1-bromo-1-phenylethane (70% based on Br_2 , 50.0 g, 0.27 mol), a liquid, *m/e* 105 (100%), 104 (70.1), 103 (34.5), 78 (26.6), 51 (25.4), 77 (25.4), 79 (14.2), and 91 (13.0); M^+ (⁷⁹Br) 184 (0.8%), M^+ (⁸¹Br) 186 (0.7%); δ (60 MHz), 7.3 (5 H, m, Ph), 5.1 (1 H, q, CH), and 2.0 (3 H, d, CH_3).

(b) **Ethyl 2-acetyl-3-phenylbutyrate.** Sodium (1.40 g, 0.061 mol) was dissolved in dry ethanol (100 ml), ethyl acetoacetate (7.94 g, 0.061 mol) and 1-bromo-1-phenylethane (11.20 g, 0.060 mol) added, and the solution refluxed for 3 h. The solution was concentrated, made up to the original volume with water, acidified, and extracted with ether. The combined extracts were washed (NaHCO_3 ; water), dried (Na_2SO_4), concentrated, and fractionally distilled: fraction 2 (116–124 °C, 0.7 Torr) was ethyl 2-acetyl-3-phenylbutyrate (62%, 10.9 g, 0.047 mol), a yellow liquid, *m/e* 105 (100%), 43 (70.4), 145 (66.6), 216 (52.8), 191 (41.5), 131 (24.9), 77 (19.0), and 161 (18.6); M^+ 234 (0.8%); the ester exists in CDCl_3 as a 1 : 1 mixture of a keto (K) and two rapidly exchanging enol (E) tautomers, δ (100 MHz), 7.2 (10 H, m, $\text{Ph}^{\text{K}} + \text{Ph}^{\text{E}}$), 4.2 (2 H, q, CH_2^{K}), 3.9 (2 H, q, CH_2^{E}), 3.6 (3 H, m, $\text{CHCH}^{\text{K}} + \text{CH}^{\text{E}}$), 2.3 (3 H, s, $\text{CH}_3\text{CO}^{\text{K}}$), 1.9 (3 H, s, $\text{CH}_3\text{CO}^{\text{E}}$), 1.3 (6 H, m, $\text{CH}_3\text{CPh}^{\text{K}} + \text{CH}_3\text{CPh}^{\text{E}}$), 1.3 (3 H, t, $\text{CH}_3\text{CH}_2^{\text{K}}$), and 0.9 (3 H, t, $\text{CH}_3\text{CH}_2^{\text{E}}$).

(c) **4-Phenylpentan-2-one.** Saponification of ethyl 2-acetyl-3-phenylbutyrate (8.31 g, 0.035 mol) by addition of 2M-KOH in 1 : 1 ethanol-water yielded, after work up, 4-phenylpentan-2-one (63%, 3.6 g, 0.022 mol), a liquid, *m/e* 105 (100%), 43 (79.0), 147 (56.6), 162 (53.8, M^+), 91 (36.4), 104 (23.7), 119 (22.6), and 117 (21.1); δ (60 MHz) 7.2 (5 H, s, Ph), 3.3 (1 H, m, CHCH_3), 2.6 (2 H, m, CH_2), 1.9 (3 H, s, CH_3CO), and 1.2 (3 H, d, CH_3CH).

(d) **1,1-Dicyano-2-methyl-4-phenylpent-1-ene.** Knoevenagel condensation of 4-phenylpentan-2-one (6.8 g, 0.042 mol) with malononitrile (3.1 g, 0.047 mol), by the method described earlier, gave a crude liquid product which was purified by bulb-to-bulb distillation (100°; 0.1 Torr) to yield 1,1-dicyano-2-methyl-4-phenylpent-1-ene (89%, 7.8 g, 0.037 mol), a liquid, *m/e* 105 (100%), 77 (11.5), 106 (8.8), 79 (7.6), 51 (5.4), 103 (5.0), 78 (4.0), and 39 (3.7); M^+ 210 (0.5%); δ (100 MHz) 7.25 (5 H, m, Ph), 3.1 (1 H, complex q, CHCH_3), 2.8 (2 H, complex d, CH_2), 2.1 (3 H, s, $\text{CH}_3\text{C:C}$), and 1.35 (3 H, d, CH_3CH).

Synthesis of 1,1-Dicyano-2,4-dimethyl-4-phenylpent-1-ene (12).—(a) **4-Methyl-4-phenylpentan-2-one.** Alkylation of benzene (132 g, 1.69 mol) with mesityl oxide (41.5 g, 0.43 mol) in the presence of anhydrous aluminium chloride (74.1 g, 0.56 mol), following the method of Hoffmann,²⁹ and subsequent fractional distillation yielded (85–100°; 2–3 Torr) 4-methyl-4-phenylpentan-2-one (58%, 43.8 g, 0.25 mol), a

* The absorption spectra of (4) in cyclohexane and acetonitrile are very similar except that in cyclohexane absorption ceases at 285 nm and in acetonitrile at 290 nm. This is in accordance with a shift to the blue of the folded c.t. band due to an increase in energy of the polar c.t. state on going to the non-polar solvent.

† During some Knoevenagel condensations acetamide was formed. In these cases reaction could be taken to completion by the addition of further portions of the catalyst mixture.

liquid, m/e 119 (100%), 43 (70.5), 91 (50.8), 118 (24.8), 176 (17.7, M^+), 41 (13.2), 77 (9.8), and 120 (9.7); δ (60 MHz) 7.3 (5 H, m, Ph), 2.7 (2 H, s, CH_2), 1.75 (3 H, s, CH_3CO), and 1.4 [6 H, s, $(\text{CH}_3)_2\text{C}$].

(b) 1,1-Dicyano-2,4-dimethyl-4-phenylpent-1-ene. Knoevenagel condensation of 4-methyl-4-phenylpentan-2-one (30.8 g, 0.17 mol) with malononitrile (9.7 g, 0.15 mol), by the method described earlier with subsequent fractional distillation yielded (140–150°; 0.5–0.6 Torr) 1,1-dicyano-2,4-dimethyl-4-phenylpent-1-ene (48%, 18.4 g, 0.082 mol), a liquid, m/e 119 (100%), 120 (11.0), 118 (9.1), 106 (1.5), 91 (1.0), 159 (0.8), 117 (0.7), and 121 (0.4); M^+ 224 (0.08%); δ (60 MHz) 7.4 (5 H, s, Ph), 2.9 (2 H, s, CH_2), 1.7 (3 H, s, CH_3C), and 1.5 [6 H, s, $(\text{CH}_3)_2\text{C}$].

Irradiations.—*Solvents.* The solvents used were purified as follows: cyclohexane (Cambrian Chemicals Ltd.) was passed at least twice through a silica gel column; acetonitrile (Fisons H.P.L.C. grade) and methylene chloride (Aldrich Gold Label Spectrofluorometric grade) were used as received; diethyl ether (B.D.H. Microanalytical grade) was distilled.

Quantum yield determinations. Quantum yields were determined in an optical bench assembly consisting of a 200-W high-pressure mercury lamp (Wotan HB0 200W), quartz condensing lenses, a Bausch and Lomb high-intensity monochromator (3-mm exit slit, 19-nm bandpass) and a quartz cell with attached degassing bulb. A photodiode (RCA 935) was used to monitor the light absorption in the cell. The system was calibrated by potassium ferrioxalate actinometry.³⁰ Solutions were degassed, by successive freeze-pump-thaw cycles, to $< 5 \times 10^{-3}$ Torr and photolyses carried out to $< 5\%$ conversion (typically 2%). Product analysis was by g.l.c. with reference to an internal standard, n-nonadecane.

Standard irradiation conditions. Unless stated otherwise the reactant solution, in a quartz vessel, was purged with nitrogen before and during irradiation by one or more 16-W low-pressure mercury lamps (Mineralight; U.V. Products Inc., San Gabriel, California).

Exploratory Irradiation of 1,1-Dicyano-2-methyl-4-phenylbut-1-ene (4). Product Identification.—A solution of (4) (3.0 g, 0.015 mol) in acetonitrile (1 000 ml) was irradiated for 160 h following the standard procedure. G.l.c. showed the formation of two products with relative retention times (min): product A (11.3), product B (16.5), starting material (19.1); and final relative concentrations: 68, 29, and 3%. Samples of A and B were isolated by preparative g.l.c. Product A, a crystalline solid, was 3,3-dicyano-2-methyl-4-phenylbut-1-ene (5), m/e 91 (100%), 65 (9.2), 92 (7.3), 39 (6.8), 41 (6.2), 55 (4.9), 95 (4.3), and 69 (4.0); M^+ 196 (0.6%); δ (100 MHz) 7.4 (5 H, s, Ph), 6.5 (1 H, s, C:CH *trans* to CH_3), 6.3 (1 H, m, C:CH *cis* to CH_3), 3.3 (2 H, s, CH_2), and 2.1 (3 H, d, CH_3); λ_{max} (CH_3CN) 251 (ϵ 140), 257 (180), 263 (160), and 267 nm (90) (Found: C, 79.5; H, 6.15; N, 14.3. $\text{C}_{13}\text{H}_{12}\text{N}_2$ requires C, 79.55; H, 6.15; N, 14.25%). Product B, a liquid, was 1-dicyanomethyl-1-methylindane (6), m/e 131 [100%, $M - \text{CH}(\text{CN})_2^+$], 115 (27.1, indanyl⁺), 130 (26.5), 129 (20.9), 91 (19.0), 128 (15.3), 66 (11.6), and 132 (10.6); M^+ 196 (3.5%); δ (100 MHz) 7.3 (4 H, m, C_6H_4), 3.70 [1 H, s, $\text{CH}(\text{CN})_2$], 3.0 (2 H, m, $\text{CH}_2\text{C}_6\text{H}_4$), 2.3 [2 H, m, $\text{CH}_2\text{C}(\text{CH}_3)$], and 1.62 (3 H, s, CH_3); λ_{max} (CH_3CN) 258 (ϵ 710), 264 (1 020), and 271 nm (1 060) (Found: C, 79.55; H, 6.15; N, 14.25. $\text{C}_{13}\text{H}_{12}\text{N}_2$ requires C, 79.55; H, 6.15; N, 14.25%).

Independent synthesis of 1-dicyanomethyl-1-methylindane

(6).—(a) 1-Dicyanovinylideneindane. Knoevenagel condensation of indan-1-one (5.0 g, 0.038 mol) with malononitrile (5.0 g, 0.078 mol) by the method described earlier gave a solid product which was recrystallised (ethanol) to yield 1-dicyanovinylideneindane (82%, 5.6 g, 0.031 mol) as fine needles, m.p. 145–146 °C (lit.³¹ 154–155 °C); m/e 180 (100%, M^+), 115 (81.4), 153 (46.0), 119 (25.9), 179 (21.2), 152 (19.5), 63 (15.0), and 118 (13.0); δ (60 MHz) 8.4 (1 H, m, aromatic H closest to CN), 7.5 (3 H, m, remaining aromatic H), and 3.2 (4 H, s, coincident CH_2 's).

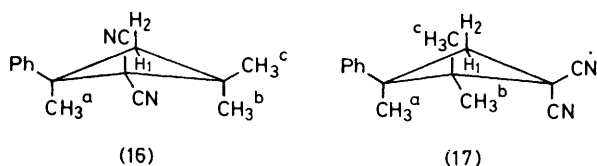
(b) 1-Dicyanomethyl-1-methylindane.³² A solution of 1-dicyanovinylideneindane (2.0 g, 0.011 mol) in dry benzene (60 ml) was added, with stirring, over a period of 40 min to a solution of methylmagnesium iodide made from magnesium turnings (0.91 g, 0.038 mol) and methyl iodide (4.36 g, 0.031 mol) in dry ether (25 ml). The resulting solution was stirred at room temperature for 1 h, poured onto 10% HCl (50 ml) and crushed ice (50 ml), the organic layer separated, and the aqueous phase extracted with benzene. The combined extracts were washed (dilute HCl; NaHCO_3 ; water), dried (Na_2SO_4), and concentrated to give an orange oil. Bulb-to-bulb distillation (160–165°; 1 Torr) yielded 1-dicyanomethyl-1-methylindane (63%, 1.36 g, 0.0070 mol), a liquid. The m.s. and n.m.r. spectrum of 1-dicyanomethyl-1-methylindane prepared in this manner were identical with those of product B in the photolysis of 1,1-dicyano-2-methyl-4-phenylbut-1-ene.

Exploratory Irradiation of 1,1-Dicyano-2-methyl-4-phenylbut-1-ene (4). Effect of Solvent Polarity.—Four solutions of (4) (7 mg, 0.36 mmol) in cyclohexane, diethyl ether, methylene chloride, and acetonitrile (each 7 ml) were placed in quartz tubes, purged with nitrogen for 30 min, and tightly stoppered. The solutions were irradiated for 20 min in a roundabout with a 400-W medium-pressure mercury lamp (Baird and Tatlock, 360/1431) through a 5-mm copper sulphate filter solution (12 g in 1 000 ml H_2O ; 100% absorbing < 270 nm). After concentration g.l.c. analysis gave the relative amounts of (5) and (6) produced. G.l.c.–m.s. confirmed peak assignments in each case. The irradiations were taken to 5–10% conversion. The ratio (6) : (5) was < 0.01 (cyclohexane), 0.09 (diethyl ether), 0.21 (methylene chloride), and 2.9 (acetonitrile).

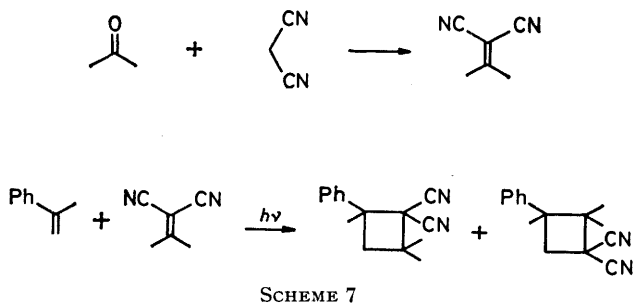
Exploratory Irradiation of 1,1-Dicyano-2-methyl-4-phenylpent-1-ene (7).—A solution of (7) (0.65 g, 3.1 mmol) in acetonitrile (100 ml) was irradiated for 25 h following the standard procedure. G.l.c. showed the formation of three products with relative retention times (min): product A (22.0), product B (27.5), product C (28.5), and starting material (30.7); and final relative concentrations: 80, 1, 11, and 8%. Samples of A and C were obtained by preparative g.l.c. and m.s. for all three products by g.l.c.–m.s. Product A, a crystalline solid, was 3,3-dicyano-2-methyl-4-phenylpent-1-ene (8), m/e 105 (100%), 104 (14.9), 106 (12.1), 77 (11.8), 79 (9.3), 103 (8.7), 51 (6.5), and 78 (6.3); M^+ 210 (not present); δ (100 MHz) 7.1 (5 H, m, Ph), 5.34 (1 H, s, C:CH *trans* to CH_3), 5.20 (1 H, m, C:CH *cis* to CH_3), 3.4 (1 H, q, CHCH_3), 1.92 (3 H, s, CH_3C), 1.6 (3 H, d, CH_3CH). Product B was an isomer of the starting material, m/e 104 (100%), 105 (41.0), 32 (39.0), 41 (18.7), 56 (17.5), 103 (17.4), 77 (15.2), and 78 (14.9); M^+ 210 (1.0%). Product C, a liquid, was 1-dicyanomethyl-1,3-dimethylindane (9), m/e 145 (100%, $M - \text{CH}(\text{CN})_2^+$), 129 (45.4, 145 – CH_3^+), 128 (22.4), 144 (19.0), 104 (18.7), 32 (15.2), 66 (14.1), and 115 (14.0); M^+ 210 (3.3%); δ (100 MHz); Fourier-transform, no integration; both possible stereoisomeric forms were

present) 7.3 (s, Ph), 3.87 [s, CH(CN)₂, I + II], 3.3 (q, CHCH₃, I), 3.0 (q, CHCH₃, II), 2.5 (m, CH₂, I + II), 1.84 [s, CH₃CCH(CN)₂, I + II], and 1.4 (d of d, CH₃CH, I + II).

Exploratory Irradiation of 1,1-Dicyano-2,4-dimethyl-4-phenylpent-1-ene (12).—A solution of (12) (0.54 g, 2.2 mmol) in acetonitrile (100 ml) was irradiated for 26 h following the standard procedure. G.l.c. (200°) showed the formation of four major products with relative retention times (min): product A (17.9), product B (20.0), product C (22.7), product D (26.1), and starting material (28.3); and final relative concentrations: 7, 13, 33, 46, and 1%. Samples of A—D were isolated by preparative g.l.c. Product A, a liquid, was 1-dicyanomethyl-1,3,3-trimethylindane (13), *m/e* 159 [100%, *M* - CH(CN)₂⁺], 143 (73.0, 1,3-dimethylindanyl⁺), 91 (46.2), 128 (42.0), 144 (40.7), 119 (29.5), 117 (29.5), and 118 (29.1); *M*⁺ 234 (3.4%); δ (100 MHz) 7.3 (4 H, m, C₆H₄), 3.84 [1 H, s, CH(CN)₂], 2.2 (2 H, m, CH₂), 1.62 (3 H, s, CH₃), 1.41 (3 H, s), and 1.36 [6 H, s, (CH₃)₂C].



Products B and C were assigned as 1-phenyl-2,2-dicyano-1,3,3- (16) and 1-phenyl-3,3-dicyano-1,2,2-trimethylcyclobutane (17), respectively, by comparison with independently synthesized samples (Scheme 7). Spectral analysis of B, a liquid gave *m/e* (15 eV) 118 [100%, Ph(CH₃)₂C:CH₂⁺], 109 (11.6), 106 [11.5, (CH₃)₂C:C(CN)₂⁺], 117 (4.5), 56 [1.6, (CH₃)₂C:CH₂⁺], 78 (1.3), 168 [1.2, Ph(CH₃)C:C(CN)₂⁺], and 103 (1.1); *M*⁺ 224 (0.3%); δ (100 MHz) 7.3 (5 H, m, Ph), 2.82 (1 H, d, *J* 12 Hz, 1-H), 2.41 (1 H, d, *J* 12 Hz, 2-H), 1.80 (3 H, s, CH₃^a), 1.60 (3 H, s, CH₃^b), and 1.39 (3 H, s, CH₃^c). Spectral analysis of C, a liquid, gave *m/e* (15 eV) 118 (100%), 146 [28.9, Ph(CH₃)C:C(CH₃)₂⁺], 119 (16.1), 106 (4.5), 131 (3.6), 147 (3.1), 32 (3.0), and 159 (2.8); *M*⁺ 224 (0.5%); δ (100 MHz) 7.25 (5 H, m), 3.24 (1 H, d, *J* 12 Hz, 1-H), 2.66 (1 H, d, *J* 12 Hz, 2-H), 1.67 (3 H, s, CH₃^a), 1.56 (3 H, s, CH₃^b), and 1.10 (3 H, s, CH₃^c).



Product D, a crystalline solid, was 2,3-dimethyl-2,3-diphenylbutane (18), *m/e* (15 eV) 119 (100%), 118 (38.7), 120 (13.6), 238 (1.9, *M*⁺), 117 (1.7), 110 (0.9), 105 (0.9), and 103 (0.9); δ (100 MHz) 7.1 (10 H, m, 2 × Ph) and 1.32 (12 H, s, 4 × CH₃). This assignment was confirmed by an independent synthesis (see below).

Analysis of Decomposition Products in Exploratory Photolysis of (12).—G.l.c. analysis (135°) showed the presence of four major, shorter retention time products. Two of these were identified as 2-phenylpropene (14) and 1,1-dicyano-2-

methylpropene (15) by g.l.c. co-injection with authentic samples.

Independent Syntheses of 1-Phenyl-2,2-dicyano-1,3,3-trimethylcyclobutane (16), 1-Phenyl-3,3-dicyano-1,2,2-trimethylcyclobutane (17), and 2,3-Dimethyl-2,3-diphenylbutane (18).—**Synthesis of (16) and (17).** A solution of 2-phenylpropene (3.0 g, 0.025 mol) and 1,1-dicyano-2-methylpropene (10.0 g 0.094 mol; prepared by the method of Prout³³) in acetonitrile (30 ml), degassed with nitrogen, was irradiated for 56 h with a 400-W medium-pressure lamp (Baird and Tatlock 360/1431). Samples of 1-phenyl-2,2-dicyano-1,3,3- (16) and 1-phenyl-3,3-dicyano-1,2,2-trimethylcyclobutane, (17) were isolated by preparative g.l.c.

Synthesis of (18). A solution of benzophenone (3.86 g, 0.022 mol) in cumene (15 g, 0.13 mol), degassed with nitrogen, was irradiated for 97 h with a 400-W medium-pressure mercury lamp (Baird and Tatlock 360/1431). A portion of the crude solid product was passed through a silica gel column, eluted with hexane. Recrystallisation (hexane) yielded 2,3-dimethyl-2,3-diphenylbutane (18) as a waxy solid.

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