Substituent Effects in the Di-π-methane Rearrangement of 1,1-Dicyano-2-methyl-3-phenylpropene

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1,1-Dicyano-2-methyl-3-phenylpropene and ring-substituted derivatives on photolysis undergo a di-π-methane rearrangement to give the corresponding cyclopropane derivatives. The effect of ring substitution on the quantum yields of these singlet state reactions can be analysed in terms of the balance between diradical and charge-transfer character on initial bonding. If the extent of charge transfer is large, efficient non-radiative relaxation of the 'zwitterion' to the ground state olefin takes place, resulting in low quantum yields for the di-π-methane rearrangement.

RECENTLY we reported[1] on the di-π-methane rearrangement of 1,1-dicyano-2-methyl-3-phenylpropene (I; X = H) and ring-substituted derivatives. Several aspects of the di-π-methane rearrangement have been analysed in detail.[2] However, one of the less studied (and less clear) aspects of the reaction is the effect of different substituents on the reactivity.[3] We present here a study of substituent effects of reaction (1).

RESULTS AND DISCUSSION

Spectroscopy.—The ionization potentials (I.P.) (Table 1) and u.v. spectra (Table 2) for a representative selection of the molecules studied are presented below, together with those of the corresponding substituted toluenes[4] and of 3,3-dicyano-2-methylpropene (DCMP).

None of the compounds studied were observed to fluoresce at room temperature in a range of solvents.

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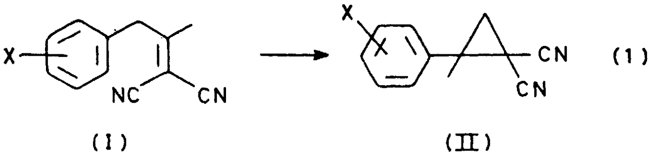
[1] R. C. Cookson, A. B. B. Ferreira, and K. Salisbury, *J.C.S. Chem. Comm.*, 1974, 665.

[2] S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 1973, **73**, 533.

[3] S. S. Hixson, *J. Amer. Chem. Soc.*, 1972, **94**, 2507.

[4] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, Chemical Rubber Co., Cleveland, 1972—1973, 53rd edn., p. E62.

Compound (I; X = H) in a 1 : 1 isopentane–methylcyclohexane glass at 77 K also showed no detectable fluorescence.



It was interesting to observe that the fluorescence of *p*-xylene, *p*-toluonitrile, and *p*-methoxytoluene (cyclohexane solutions) were very efficiently quenched by DCMP. The slopes of the Stern–Volmer plots were, respectively, 5.6 × 10², 3.3 × 10², and 2.0 × 10² l mol⁻¹.

TABLE 1

Ionisation potentials of selected compounds

Compound (I)	I.P. (eV)	$XC_6H_4CH_3$	I.P. (eV)
X = *p*-CN	9.79	*X* = *p*-CN	9.76
X = H	9.41	X = H	8.82
X = *p*-Me	9.00	X = *p*-MeO	8.44
X = *m*-MeO	8.65	X = *m*-MeO	8.31
X = *p*-MeO	8.51	X = *p*-MeO	

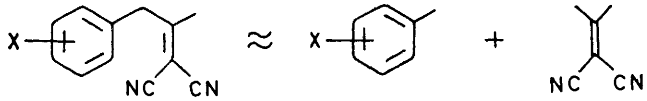
DCMP, I.P. = 10.21 eV.

TABLE 2

U.v. absorption spectra of (I) in cyclohexane

Compound (I)	$\lambda_{max.}$ or shoulder/nm (ε/l mol⁻¹ cm)
X = *p*-CN	260 (7 200), 270 (2 000), 281 (720)
X = H	260 (4 800), 266 (4 000), 273 (2 800)
X = *p*-Me	271 (3 800), 277 (3 600)
X = *p*-MeO	278 (3 700), 286 (3 900)
X = *p*-Cl	273 (3 200), 280 (2 100)

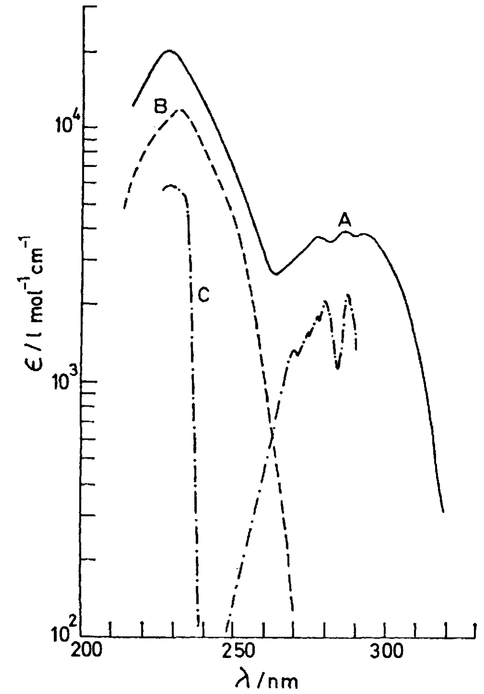
DCMP, $\lambda_{max.}$ 232 nm(ε 1 1200).



The molecules (I) can be considered as being composed of two chromophores, aromatic and olefinic. In this sense, substituted toluenes and DCMP would be models for the chromophores. It is known that two chromophores united by a methylene bridge to form a molecule quite commonly show strong interaction.[5]

From Table 1 it can be seen that there is a stabilizing ground-state interaction for compounds (I), as measured by the difference in I.P. between compounds (I) and the corresponding substituted toluene with the same substituent X. It is relevant that the only exception is for X = *p*-CN, suggesting that this stabilizing influence is the result of a ground-state, charge-transfer interaction.

The strong fluorescence quenching observed for mixtures of substituted toluene and DCMP probably derives from an interaction which is largely charge transfer in character resulting in a net transfer of change from the aromatic ring to the olefinic double bond.[6] From the Stern–Volmer slopes (*s*) and the fluorescence lifetimes [7] (τ_F), the quenching constants (k_q) can be obtained, $k_q = s/\tau_F$. The k_q values increase with the electron-donor character of the substituent in the fluorescer; this is consistent with change-transfer character in the exciplex. But the k_q values are all larger than the diffusion rate constant ($k_{diff.}$) for the solvent, cyclohexane, at 25 °C [8] ($k_{diff.}$ *ca.* 1.1 × 10¹⁰ l mol⁻¹ s⁻¹). This might be an indication of a ground-state complex but it would be very weakly held, since none of the solutions used for fluorescence quenching show appreciable departure from additivity in their u.v. spectra. Indeed, it may well be that quenching studies of this type provide an extremely sensitive probe for weak ground state interactions between solutes. Analysis of the



U.v. spectra of A, (I; X = *p*-MeO); B, DCMP; C, *p*-$MeOC_6H_4CH_3$

TABLE 3

Quenching rate constants for quenching toluene derivatives by DCMP

Fluorescer	*s*/l mol⁻¹	$10^9\tau$/s	k_q/ l mol⁻¹ s⁻¹
p-Toluonitrile	3.3 × 10²	19	1.7 × 10¹⁰
p-Xylene	5.6 × 10²	30	1.9 × 10¹⁰
p-Methoxytoluene	2.0 × 10²	8.7	2.3 × 10¹⁰

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[5] (*a*) F. C. De Schryver and J. Put, *Bull. Soc. chim. belges*, 1972, **37**, 1107; (*b*) R. Foster, 'Organic Charge-transfer Complexes,' Academic Press, London, 1969, p. 78.

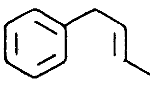
[6] (*a*) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1972, **94**, 3679; (*b*) M. P. Niemczyk, M. E. Schore, and N. J. Turro, *Mol. Photochem.*, 1973, **5**, 69; (*c*) N. J. Turro, C. Lee, N. E. Schore, J. Barltrop, and H. A. J. Carless, *J. Amer. Chem. Soc.*, 1971, **93**, 3079.

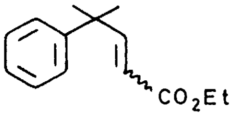
[7] (*a*) S. L. Murov, 'Handbook of Photochemistry,' Dekker, New York, 1973, p. 21; (*b*) Obtained by single photon counting, P. M. Crosby, personal communication; (*c*) I. Berlman, 'Handbook of Fluorescence Spectra of Aromatic Molecules,' Academic Press, New York, 1965, p. 68.

[8] Ref. 7*a*, p. 55.

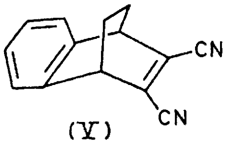
u.v. spectra is facilitated by considering some related molecules (III)—(V).

In (III) the two chromophores behave as if they were virtually isolated: the u.v. spectrum is additive (for $\lambda > 220$ nm); the fluorescence quantum yield and singlet lifetime are similar to those of toluene.[9] For (IV) the u.v. spectrum around 260 nm resembles that of cumene, but for $\lambda < 250$ nm there is a strong departure from additivity, with enhanced absorption. This is assigned [10] to direct excitation into a delocalized state formed by mixing the αβ-unsaturated ester chromophore π–π* state with higher excited states (S_2 or S_3) of the benzenoid chromophore. The spectrum of (V) gives $\lambda_{max.}$ 239 (ε 6 700), 267sh (650), and 278sh nm (650). This is interpreted [11] as being the combination of a charge-transfer band (with the benzenoid absorption superimposed) at longer wavelengths, and a second band corresponding to the dicyanoethylene chromophore (at 239 nm).


(III)



(IV)



(V)

For compounds (I) we propose the existence of a charge-transfer state, close in energy to the benzenoid S_1 state, but probably slightly higher. Mixing of benzenoid upper states and the olefinic π–π* state does not seem substantiated by the spectra.

Reactivity.—The quantum yields of reaction (1) for a wide range of substituents X in cyclohexane solutions, and for a restricted number of substituents, in other solvents, are given in Table 4, relative to (I; X = H) in cyclohexane (ϕ_Δ^{rel}). The quantum yield (ϕ_Δ) of the 'parent' compound of the series (I; X = H) in cyclohexane is 1.8×10^{-2}. This reaction could not be sensitized by triplet energy transfer from xanthone or *p*-methoxytoluene, under conditions where efficient transfer to *trans*-1-cyano-2-methyl-3-phenylpropene occurred (as demonstrated by *trans–cis* isomerization).

TABLE 4

Quantum yields of reaction of (I)

	ϕ_Δ^{rel}			
Substituent (X)	Cyclohexane	Dioxan	CH_2Cl_2	MeCN
p-CN	4.0	3.0		2.0
p-Cl	1.2			
P-Br	1.2			
H	1.0	0.70	0.62	
p-Me	0.49			
m-MeO	0.11			
p-MeO	0.10	0.01		0.01

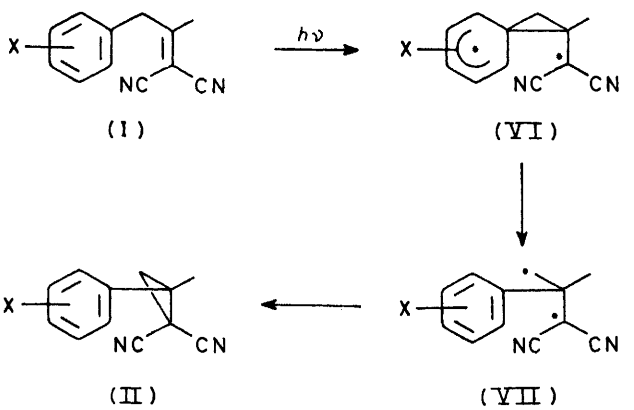
Irradiation of 1,1-dicyano-2-methyl-3-(α-naphthyl)-propene in cyclohexane did not lead to detectable amounts of the corresponding cyclopropane ($\phi_\Delta < 2 \times 10^{-5}$) and the material was quite photostable.

Although the solutions irradiated were routinely degassed, the quantum yields for air-saturated solutions were not significantly different.

The major problem that occurs in analysing the reactivities of a non-fluorescent series of compounds is the inability to obtain accurate reaction rate constants. Reluctantly, we are forced to examine trends in the quantum yields.

The lack of reactivity of the triplet states of the series gives clear evidence for a singlet state process and the activating influence of the terminal cyano groups is evident. 1-Phenylbut-2-ene does not show the di-π-methane rearrangement in the liquid phase.[12] According to current ideas on this rearrangement,[2] the increase in reactivity is due to stabilization of an intermediate stage represented by (VI).

Even more striking is the correlation between the reaction quantum yields (in cyclohexane) and the electron withdrawing–donating properties of the substituents. A plot of log ϕ_Δ^{rel} *versus* σ^+ for the *para*-substituents gives a slope ρ of 1.2 (correlation coefficient *r* 0.971). This seems to contradict what might be an intuitively plausible alternative (or contributing structure) for (VI), a polarized species such as (VIII). On the other hand, such species might be considered as representing a limiting case of the intramolecular analogue of the exciplexes formed intermolecularly between substituted



SCHEME 1

(VIII)

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[9] (*a*) H. Morrison and R. Peiffer, *J. Amer. Chem. Soc.*, 1968, **90**, 3428; (*b*) H. Morrison, J. Pajak, and R. Peiffer, *ibid.*, 1971, **93**, 3978.

[10] D. DeKeukeleire, E. C. Sanford, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1973, **95**, 7904.

[11] R. C. Cookson, J. Dance, and M. Godfrey, *Tetrahedron*, 1968, **24**, 1529.

[12] (*a*) Ref. 9*a*; (*b*) C. S. Nakagawa and P. Sigal, *J. Chem. Phys.*, 1970, **52**, 3277; (*c*) see also for gas-phase work, M. Comtet, *J. Amer. Chem. Soc.*, 1970, **92**, 5308.

toluenes and DCMP. Formation of this exciplex would deactivate the excited (I) and compete with the di-π-methane rearrangement. Moreover, the molecular motion leading to (VIII) is the same as that leading to (VI): this could be considered as a form of the ' touching decay ' mechanism of deactivation proposed by Zimmerman.[13]

Formation of exciplexes (as measured by the rate constant k_E) for a fixed electron acceptor and varying donors is known to depend on the ionization potential of the donor (I.P.) through a relationship of the form log $k_E = a + b$(I.P.).[6] And the ionization potentials of substituted benzenes are linearly related to the Hammett substituent constants,[14] both measuring electron availability.

Hence, the correlation between the di-π-methane rearrangement quantum yields and substituent constants can be minimally attributed to the competing excited-state deactivation through exciplex formation.

Another experimental observation that can be explained by enhanced exciplex formation is the decrease in reaction quantum yields with increasing solvent polarity. Significantly this effect is more pronounced in the case where the exciplex should be more easily formed [*i.e.* for (I; X = *p*-MeO)]. The lack of reactivity of 1,1-dicyano-2-methyl-3-(α-naphthyl)propene can be tentatively explained by the low I.P. of the naphthyl chromophore (enhanced exciplex formation), and its low excited singlet energy (less energy available to overcome barriers in the reaction pathway).

EXPERIMENTAL

Instrumentation.—G.l.c. was carried out on a Pye–Unicam 104 instrument, fitted with ¼ in glass columns, using OV-1 (or SE 30) or occasionally QF-1 as the liquid phase. Preparative g.l.c. was performed on a Pye–Unicam 105 or 104 instrument with collection adaption; preparative columns were ⅜ or ½ in, made of glass. N.m.r. spectra were taken on a Perkin-Elmer R12 (60 MHz) instrument for routine analysis and on Varian HA-100 (100 MHz) with optional computer averaging of transients or Varian XL-100 (100 MHz Fourier transform) spectrometers for small samples. The solvent used was $CDCl_3$. The chemical shifts are from internal tetramethylsilane. Mass spectra were taken on an A.E.I. MS-12 instrument, fitted for most of the analysis with a Digispec PDP-8 data system; i.r. spectra on Perkin-Elmer 157G and Pye–Unicam 200G instruments; u.v. spectra on Pye–Unicam SP 800A and Perkin-Elmer 402 spectrophotometers; photoelectron spectra on a Perkin-Elmer PS 18 instrument; and fluorescence spectra on a Farrand Mk 1 machine, with or without corrected spectra attachment.

Irradiations.—All solutions used for photolysis were either degassed by at least three cycles of freeze–pump–thaw or deoxygenated by purging with oxygen-free nitrogen for 30 min prior to irradiation. All quantum yields were measured at 254 nm and at <10% conversion.

The quantum yield of reaction (1) for X = H was determined in an optical bench system calibrated with potassium ferrioxalate.[15] For the other substituents the relative quantum yields were determined using (I; X = H) as a secondary actinometer, in a roundabout apparatus. The use of (I; X = H) as a secondary actinometer can be justified in view of: (a) in the range of concentrations investigated (5×10^{-4}—5×10^{-3}M) no dependence of the quantum yield of reaction (1) for X = H with concentration was observed; (b) the product (II; X = H) is quite inert (quantum yield of any reaction is $<10^{-4}$) and its extinction coefficient at 254 nm is <5% of that of (I; X = H); (*c*) (I; X = H) and (II; X = H) can be easily separated on g.l.c. using OV-1 columns and using n-octadecane as a convenient inert internal standard. The triplet sensitizers used were fluorenone, xanthone, and *p*-methoxytoluene (E_T 53, 74, and 76 kcal mol^{-1}, respectively.

The solvents were purified as follows. Cyclohexane (spectroscopic grade) was percolated through a SiO_2 column and distilled. 1,4-Dioxan was distilled from KOH, then from Na, under nitrogen. Acetonitrile and methanol were spectrofluorometric and spectroscopic grades, respectively, and used as received. Dichloromethane was treated with Na_2CO_3, dried ($MgSO_4$), and distilled. All the purified solvents were transparent at 254 nm.

TABLE 5

N.m.r. spectrum of compounds (II)

Substituent	Aromatic	CH_2 [a]	CH_3	Other
H	7.39 (5 H, s)	2.22 (1 H, d, *J* 6 Hz) 1.96 (1 H, d, *J* 6 Hz)	1.78 (3 H, s)	
p-CH_3	7.20 (4 H, s)	2.28 (1 H, d, *J* 6 Hz) 1.94 (1 H, d, *J* 6 Hz)	1.72 (3 H, s)	2.30 (3 H, s, ring Me)
p-CN	7.60 (4 H, centre of AA′BB′)	2.32 (1 H, d, *J* 7 Hz) 2.04 (1 H, d, *J* 7 Hz)	1.80 (3 H, s)	
p-MeO	7.08 (4 H, centre of AA′BB′)	2.30 (1 H, d, *J* 6 Hz) 1.92 (1 H, d, *J* 6 Hz)	1.76 (3 H, s)	3.78 (3 H, s, ring MeO)
m-MeO	6.72, 7.14 (m)	2.16 (d, *J* 6 Hz) 1.78 (d, *J* 6 Hz)	1.70 (s)	3.71 (s, (ring MeO)

[a] The two methylene doublets were shown to be coupled by double irradiation experiments.

TABLE 6

Mass spectral data for compounds (II)

X	*m/e*
H	183 (17%, $M^{+\cdot}$ +1), 182 (100, $M^{+\cdot}$), 181 (76, $M^{+\cdot}$ −H·), 167 (57, $M^{+\cdot}$ −CH_3·), 140 (68, $M^{+\cdot}$ −42), 91 (90, $C_7H_7^+$)
p-CH_3	197 (6%, $M^{+\cdot}$ +1), 196 (42, $M^{+\cdot}$), 181 (100, $M^{+\cdot}$ −15), 154 (49, $M^{+\cdot}$ −42)
p-MeO	213 (9%, $M^{+\cdot}$ +1), 212 (57, $M^{+\cdot}$), 197 (100, $M^{+\cdot}$ −15), 170 (17, $M^{+\cdot}$ −42) [a]
m-MeO	213 (17.3%, $M^{+\cdot}$ +1), 212 (100, $M^{+\cdot}$), 211 (25, $M^{+\cdot}$ −H·), 197 (62%, $M^{+\cdot}$ −15)

[a] Heated probe.

Product Analysis and Identification.—The irradiated solutions were analysed by g.l.c. on a 20 ft 5% OV-1 column.

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[13] H. E. Zimmerman, D. P. Werthermann, and K. S. Kamm, *J. Amer. Chem. Soc.*, 1974, **96**, 439.

[14] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, ' Molecular Photoelectron Spectroscopy,' Wiley, London, 1970, ch. 11.

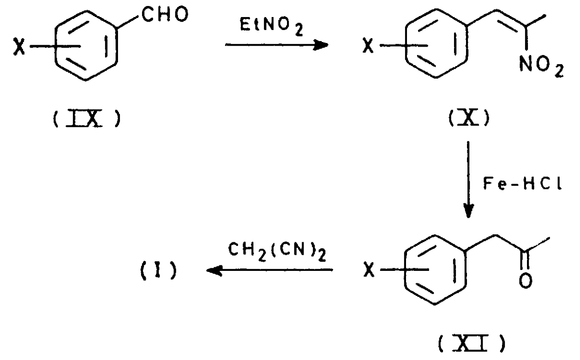
[15] C. A. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, **A235**, 518.

In all cases the cyclopropane product has a smaller retention time than the starting material. The ratio of retention times is 0.83 ± 0.02 in all cases. Compounds (II; X = H, *p*-CN, *p*-Me, *p*-MeO, and *m*-MeO) were isolated from preparative scale photolyses. Compound (II; X = H) was also synthesised independently. Identification through n.m.r. spectra was quite unambiguous and mass spectra provided further confirmation. Other data were also obtained in some cases, mainly to exemplify basic features. Compound (II; X = *p*-CH_3) had $\lambda_{max.}$ (cyclohexane) 259 (ε 233), 265 (265), and 271 nm (164); (II; X = H) had $\lambda_{max.}$ (cyclohexane) 255 (ε 190), 261 (230), 267 (190), and 270 nm (120).

TABLE 7

Synthesis of β-nitrostyrene derivatives

Substituent	Solvent	Base	*t*/day	Temperature	Yield (%)	Separation method
m-MeO		$EtNH_2$	10	Room	61	Distillation (0.15 Torr; 122—138 °C)
p-CN	EtOH	$EtNH_2$–Bu^nNH_2	3	Reflux	21	Crystallisation
p-Me	EtOH	$EtNH_2$	5	Room	39	Crystallisation
p-Br	EtOH	Bu^nNH_2	1	Reflux	68	Crystallisation
p-Cl	EtOH	Bu^nNH_2	1	Reflux	30	Crystallisation



SCHEME 2

In the case of (II; X = *p*-Cl and *p*-Br) identification was made by their retention times on g.l.c. [and the ratio to the retention times of (I; X = *p*-Cl and *p*-Br), respectively] and by coupled m.s.–g.l.c., which gave the following results, (II; X = *p*-Br), *m/e* 262 [14%, $(M + 2)^{+\cdot}$], 261 [6, $(M\cdot + 2 -H)$ and $(M^{+\cdot} + 1)$], (181, $M^{+\cdot}$ −Br·), 166 (37), and 154 (82); (I; X = *p*-Br) (for comparison in the same run), *m/e* 263 [11%, $(M + 2)^{+\cdot} - 1$], 262 [86 $(M + 2)^{+}$], 260 (88, $M^{+\cdot}$), 181 (67, $M^{+\cdot}$ − Br·), 166 (38), and 154 (100); (II; X = *p*-Cl), *m/e* 218 [9%, $(M + 2)^{+\cdot}$], 217 [7, $(M + 2)^{+\cdot}$ −H· and $M^{+\cdot} + 1$], and 181 (100, $M^{+\cdot}$ −Cl); and (II; X = *p*-Cl) (for comparison in the same run), *m/e* 219 [4%, $(M + 2)^{+\cdot} + 1$], 218 [32; $(M + 2)^{+\cdot}$], 216 (100, $M^{+\cdot}$), 215 (43, $M^{+\cdot}$ − H·), 181 (68, $M^{+\cdot}$ − Cl), and 154 (45).

Synthesis of (I).—The steps in Scheme 2 were generally followed. The ketone (XI; X = H) is commerically available. The detailed procedure for each step is exemplified here for X = *p*-MeO; the main reaction parameters for the other substituents are also given.

Synthesis of β-nitrostyrene derivatives. This type of reaction can be performed in a large number of ways as regards solvent system, base, *etc.*[16] The procedure described here was used by Pepper and Saha.[17] Anisaldehyde (66.2 ml, 75 g), nitroethane (41 ml, 41.2 g), ethylamine (75 drops, 70% solution in water), and absolute ethanol (50 ml), were mixed in a flask. After 6 days, the mixture was cooled (which caused it to solidify), filtered, and the yellow crystals washed with dilute H_2SO_4 and H_2O. After drying under vacuum, crstyals (58.5 g, 55%) were obtained, which could be recrystallised from MeOH–H_2O.

Synthesis of arylacetone derivatives. 1-(*p*-Methoxyphenyl)-2-nitropropene (40 g), iron powder (87 g), $FeCl_2(H_2O)_X$ (3.5 g), ethanol (350 ml), and water (400 ml) were warmed in a flask with reflux condenser and mechanical stirrer. When warm, concentrated HCl was added in one batch.[17] After reflux with stirring for 5 h, the mixture was filtered in a Buchner funnel, with suction, the solid washed with hot ethanol, and the filtrate evaporated in a rotary evaporator. After repeating the filtration step and concentrating further, the residual liquid was distilled under vacuum. A liquid (18.3 g, 54%), b.p. 126 °C at *ca.* 1 Torr, was obtained.

TABLE 8

N.m.r. data for compounds (X)

	Chemical shift δ			
Substituent	Olefinic (1 H)	Aromatic (4 H)	Allylic (3 H)	Other
p-MeO	7.92	6.8—7.35	2.32	3.71 (OMe)
m-MeO	7.90	6.7—7.5	2.30	3.73 (OMe)
p-CN	8.10	7.5—8.0	2.47	
p-Me	7.98	7.3	2.37	2.37 (*p*-Me)
p-Br	7.98	7.1—7.7	2.40	
p-Cl	8.03	7.4	2.43	

TABLE 9

Synthesis of arylacetone derivatives

Substituent	Yield (%)	Isolation method
m-MeO	36	Distilled at 85 °C and *ca.* 0.1 Torr
p-CN	50	Distilled at 150 °C and 0.1 Torr
p-Br	63	Distilled at 110 °C and 0.3 Torr
p-Me	55	Distilled at 70 °C and 0.3 Torr
p-Cl	68	Distilled

TABLE 10

N.m.r. data for arylacetone derivative

	Chemical shift δ			
Substituent	Aromatic (4 H)	Methylene (2 H)	Methyl (3 H)	Other
p-MeO	6.50—7.25	3.57	2.05	3.72 (OMe)
m-MeO	6.10—6.90	3.02	1.46	3.08 (OMe)
p-CN	7.20—7.90	8.81	2.22	
p-Br	6.98—7.58	3.64	2.15	
p-Cl	6.95—7.45	3.63	2.11	

Synthesis of (I). Using ammonium acetate as catalyst (1.39 g) and benzene (31 ml)–glacial acetic acid (47 drops)

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[16] G. Jones, 'Organic Reactions,' Wiley, New York, 1967, vol. 15, p. 204; O. Schales and H. A. Graeffe, *J. Amer. Chem. Soc.*, 1952, **74**, 4486; G. B. Gairaud and G. R. Lappin, *J. Org. Chem.*, 1953, **18**, 3.

[17] J. M. Pepper and M. Saha, *Canad. J. Chem.*, 1964, **62**, 113.

as solvent system,[18] *p*-methoxyphenylacetone (15.1 g) and malononitrile (6.1 g) were refluxed in a flask fitted with a Dean–Stark head. After *ca.* 15 h water (2 ml) was collected and the supernatant benzene was clear. After separating the layers, washing the organic layer with H_2O, 1N-$NaHCO_3$, and H_2O, drying, and evaporating the solvent, the residue was distilled; the first and second fractions (78%), b.p. 136 °C at *ca.* 0.1 Torr) gave a colourless liquid.

TABLE 11

Synthesis of compounds (I)

Substituent	Yield (%)	Isolation (besides final purification)
H	55, 89	Distilled at 104 °C and 0.2 Torr
m-MeO	61	Distilled at 135 °C and 0.1 Torr
p-CN	98	Crystallised, m.p. 107—108 °C [b]
p-Me	~60	Distilled at 132 °C and 0.25 Torr
p-Br	~90 [a]	Preparative g.l.c.
p-Cl	~90 [a]	Preparative g.l.c.

[a] Yield before isolation. [b] From benzene–light petroleum.

TABLE 12

N.m.r. data of compounds (I)

Substituent	Chemical shift δ Aromatic	CH_2	CH_3	Other
H	7.10—7.45 (5 H, s)	3.87 (s)	2.19 (s)	
p-MeO	6.99 (4 H, centre of AA′BB′)	3.82 (s)	2.18 (s)	3.82 [a] (3 H, s, OCH_3)
m-MeO	6.55—7.40 (4 H, m)	3.82 (s)	2.18 (s)	3.80 (3 H, s, OCH_3)
p-CN	7.50 (4 H, centre of AA′BB′)	3.92 (s)	2.22 (s)	
p-Me	7.12 (4 H, centre of AA′BB′)	3.82 (s)	2.17 (s)	2.34 (3 H, s, Me)
p-Cl	7.25 (4 H, centre of AA′BB′)	3.82 (s)	2.17 (s)	
p-Br	7.62 (4 H, centre of AA′BB′)	3.78 (s)	2.16 (s)	

[a] Integrates to 5 H, together with CH_2.

TABLE 13

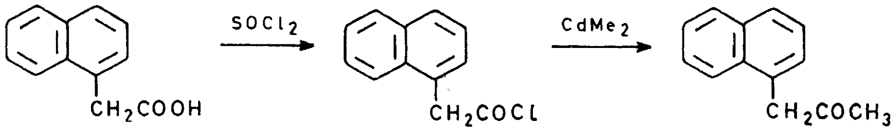
Mass spectra data for compounds (I)

Substituent	*m/e*
H	183 (13%, $M^{+\cdot}$ +1), 182 (100, $M^{+\cdot}$), 181 (79, $M^{+\cdot}$ −H·), 167 (33, $M^{+\cdot}$ −CH_3·)
p-MeO	213 (19%, $M^{+\cdot}$ +1), 212 (100, $M^{+\cdot}$), 197 (67, $M^{+\cdot}$ −CH_3), 169 (37, $M^{+\cdot}$ −43), 121 (71, $MeOC_7H_6^+$)
m-MeO	213 (18%, $M^{+\cdot}$ +1), 212 (100, $M^{+\cdot}$), 197 (19, $M^{+\cdot}$ −CH_3·), 121 (24, $MeOC_7H_6^+$)
p-CN	208 (15%, $M^{+\cdot}$ +1), 207 (100, $M^{+\cdot}$), 206 (63, $M^{+\cdot}$ −H·), 192 (38, $M^{+\cdot}$ −CH_3·)
p-CH_3	197 (14%, $M^{+\cdot}$ +1), 196 (100, $M^{+\cdot}$), 195 (61, $M^{+\cdot}$ −H·), 181 (73, $M^{+\cdot}$ −CH_3·)
p-Cl	219 (4%, $M^{+\cdot}$ +1), 218 (31, $M^{+\cdot}$), 216 (100, $M^{+\cdot}$), 181 (69, $M^{+\cdot}$ −Cl·)
p-Br	262 (11%, $M^{+\cdot}$ +1), 262 (87, $M^{+\cdot}$), 262 (87, $M^{+\cdot}$), 260 (90, $M^{+\cdot}$), 181 (66, $M^{+\cdot}$ −Br·)

U.v. spectra of compounds (I) for cyclohexane solution were as follows: X = H, $\lambda_{max.}$ 245sh (ε 11 000), 260sh (4 800), 266 (4 000), and 273 nm (2 800); *p*-MeO, $\lambda_{max.}$ 278 (ε 3 700), 286 (3 900), and 291sh nm (3 800); *p*-CN, $\lambda_{max.}$ 281 nm (ε 720); *m*-MeO, $\lambda_{max.}$ 281 nm (ε 2 100); *p*-Me, $\lambda_{max.}$ 271 (ε 3 800) and 277 nm (3 600); *p*-Cl, $\lambda_{max.}$ 273 (ε 3 200) and 280 nm (2 100); *p*-Br, $\lambda_{max.}$ 274 (ε 3 600) and 281 nm (2 600).

Synthesis of 1,1-*Dicyano*-2-*methyl*-3-(α-*naphthyl*)*propene*.—Although the last step in the preparation of this compound was the same as for (I), the required ketone (XVIII) was obtained in a different way. The method used is described by Shirley.[19] α-Naphthylacetic acid (13.07 g) was treated with thionyl chloride (26.55 g; redistilled) and the mixture stirred under reflux for 1 h (protected against moisture). Bulb-to-bulb vacuum distillation gave a reddish liquid (12.78 g, 89%) with the right spectral properties.

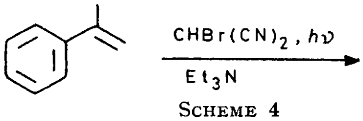
Magnesium turnings (1.508 g) in sodium-dried Et_2O (100 ml) and of methyl iodide (8.68 g) in sodium-dried Et_2O (30 ml) were used to produce MeMgI. To this Grignard reagent, anhydrous cadmium chloride (5.97 g) was added, little by little at *ca.* 0 °C and with stirring. After warming to room temperature, the mixture was stirred for 2 h. (Gilman test[20] showed the absence of Grignard reagent). Ether was distilled off, while being substituted by benzene (*ca.* 150 ml). To the white slurry of $CdMe_2$, the acid chloride (12 g) was quickly added. The mixture was refluxed for 2 h with stirring under argon. Then water (150 ml) and 1N-HCl (100 ml) were added. This was extracted with Et_2O, dried, and evaporated. The residue was bulb-to-bulb distilled at reduced pressure. G.l.c. analysis showed 90% pure product which was further purified by column chromatography on SiO_2 using $CHCl_3$–cyclohexane (50 : 50 to 100 : 0) to give a liquid (5.01 g, 57%; overall 51%) with the correct spectral properties. Further treatment as above gave 1,1-dicyano-2-methyl-3-(α-naphthyl)propene, δ 7.25—8.00 (7 H, m, ArH), 4.36 (s, CH_2), and 2.08 (s, CH_3); *m/e* 2.33 (18%, $M^{+\cdot}$ + 1), 232 (100 $M^{+\cdot}$), 231 (25, $M^{+\cdot}$ −H·), 217 (26, $M^{+\cdot}$ −CH·), 203 (11), 190 (24, $M^{+\cdot}$ − 42), 167 (24), 152 (8), 141 (25), 128 (10, $C_{10}H_7CH_2^+$), 115 (14), 63 (6), and 51 (3); $\lambda_{max.}$ (C_6H_{12}) 273 (ε 6 800), 283 (7 600), 294 (5 800), and 324 nm (1 100).



(XVIII)

SCHEME 3

Synthesis of Compound (II; X = H).—The procedure of Boldt *et al.*[21] was followed. Bromodicyanomethane was prepared by dropwise addition, under nitrogen and at 0 °C of Br_2 (32 g) to powdered malononitrile (13.2 g) in



(II)

SCHEME 4

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[18] H. O. House, ' Modern Synthetic Reactions,' Benjamin, New York, 1972, 2nd edn., p. 494.

[19] D. A. Shirley, ' Organic Reactions,' Wiley, New York, 1954, vol. 8, p. 44.

[20] H. Gilman, ' Organic Chemistry,' Wiley, New York, 1943, 2nd edn., vol. 1, pp. 489—580.

[21] P. Boldt, L. Schulz, and J. Etzemuller, *Chem. Ber.*, 1967, **100**, 1281.

water (150 ml). After stirring for 4 h, the mixture was filtered and washed with water, dried under vacuum, recrystallised from carbon tetrachloride and dried again, m.p. 61.5—62.5 °C. Bromodicyanomethane (9.8 g) in methylene chloride (20 ml) was placed in a Pyrex flask fitted with stirrer, condenser, thermometer, and bubbler to maintain a nitrogen atmosphere, and illuminated by an Osram MBW-U long wavelength u.v. lamp. α-Methylstyrene (10 g; distilled under nitrogen) in methylene chloride (20 ml) was added dropwise, so as to keep the temperature below 32 °C. The disappearance of the styrene was followed by g.l.c. (10 ft 2% OV-1; 150 °C). After the rate of decrease of styrene stabilised, 19 ml of a solution of Et_3N (30.5 ml) in CH_2Cl_2 (20 ml) was added, keeping the temperature <15 °C with an ice-bath. G.l.c. analysis showed the appearance of a peak with the expected retention time. Column chromatography (SiO_2–$CHCl_3$) to remove polymers and unchanged styrene was followed by distillation; the third fraction gave an oily solid (2 g, 16%), b.p. 115—117 °C at 0.35 Torr), with the correct n.m.r. spectrum.

TABLE 14

Yields from the photolysis of compounds (I)

Substituent	Yield of cyclopropane (%)	Remainder (%)
X = *p*-CN	82	Trace
X = H	64	Trace
X = *p*-MeO	15	7
X = *p*-CH_3	45	Trace
X = *m*-MeO	15	Trace

The yields of the other compounds (II) obtained were good except for the methoxy-substituted compounds (Table 14).

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