The Photochemistry of 1-Cyano-2-methyl-3-phenylpropene and Ring-substituted Derivatives

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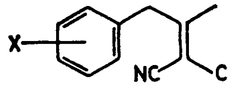
The *E*- and *Z*-isomers of 1-cyano-2-methyl-3-phenylpropene and ring-substituted derivatives of the *E*-isomer, are shown to fluoresce and undergo *Z*–*E*-isomerization and di-π-methane rearrangement on irradiation. The rate constants for these processes, obtained from fluorescence lifetimes and quantum yields, can be analysed in terms of an initial interaction between the two π systems, facilitated by partial charge-transfer, followed by two diverging pathways, one, towards a diradicaloid species leading to cyclopropane formation, the other towards a ' zwitterionic ' species and relaxation to the ground state and resulting in singlet state *Z*–*E*-isomerization.

THE photochemistry of 3-aryl-1,1-dicyano-2-methylpropenes (I) was recently reported.[1] Although the reaction quantum yields for the di-π-methane rearrangement of these compounds show an interesting correlation with the electron donating–withdrawing properties of the substituents X, we were unable to extend our studies since the lack of fluorescence prevented an analysis of the photophysics of the system.

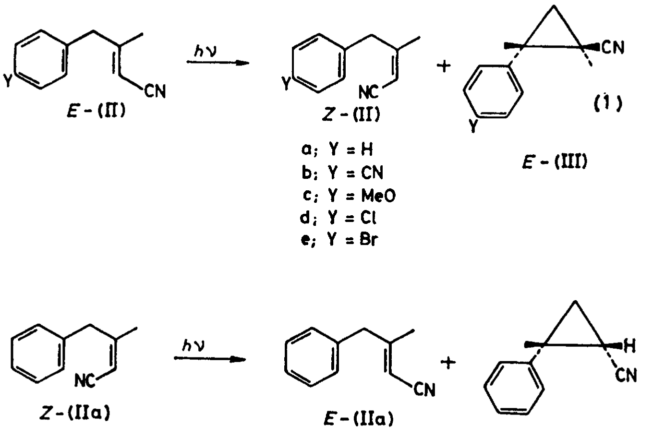


(I)

We present here a reactivity study on a related system (II), the members of which show detectable fluorescence.

RESULTS AND DISCUSSION

Photochemistry of E- *and* Z-*1-Cyano-2-methyl-3-phenylpropene* E-(IIa) *and* Z-(IIa).—The results of photolysis of *E*- and *Z*-(IIa) in cyclohexane are given in Table 1, together with spectral data.



FIGURE

Due to the difficulty in analysing the irradiated mixtures (see Experimental section), conversions were of *ca.* 10% starting material. Under these conditions, a small proportion (less than 10%) of the cyclopropanes formed did not retain the stereochemistry indicated. Since the olefinic isomer formed during photolysis will also rearrange, and the cyclopropanes (whose extinction coefficients are comparable to those of the starting olefins) can suffer photochemical interconversion, we assigned the total yield of cyclopropane to the preferred isomer.[2]

In support of this last point, irradiation of *E*-(IIIa) in cyclohexane gave Z-(IIIa) as the sole product (ϕ 0.04). Triplet (acetone) sensitization also causes interconversion.

TABLE 1

Spectral data and quantum yields for reactions of *E*- and *Z*-(IIa)

	Absorption [a]		Fluorescence [a]			Quantum yields [b]	
Compound	$\lambda_{max.}$/nm	ε	$\lambda_{max.}$/nm	ϕ_f	τ/ns [c]	ϕ_{isom}	ϕ_{cp}
E-(IIa)	261	270	285	0.004	1.0	0.090	0.019
Z-(IIa)	261	350	285	0.000 9		0.15	0.012

[a] Cyclohexane solutions; the spectra resemble that of toluene. [b] Quantum yields of olefin isomerization and cyclopropane formation, respectively. [c] Lifetime from fluorescence decay measured by single photon counting. We thank Dr. D. Phillips for the use of his group's single photon counting equipment and Dr. K. Ghiggino for help with the measurements.

Sensitized irradiation of *E*-(IIa) (using xanthone, *p*-methoxytoluene, and *p*-xylene; E_T 310, 326, and 336 kJ mol^{-1}, respectively [3]) resulted only in *E*–*Z*-isomerization, giving a photostationary state composition of 45.0% *Z*-isomer in all cases. It is known [2] that non-constrained di-π-methane systems tend to rearrange from the singlet state.[4]

The fluorescence lifetime of *Z*-(IIa) could not be reliably measured directly. It can be estimated, with help of expression (1),[5] to be 0.2 ns. τ_0^Z/τ_0^E, the ratio of

$$\tau^Z = \phi_f^Z(\tau_0^Z/\tau_0^E)(\tau^E/\phi_f^E) \qquad (1)$$

the natural lifetimes, can be obtained from the absorption spectra. All other parameters in equation (1) were measured experimentally.

From the absorption and emission spectra of *E*- and *Z*-(IIa), it can be seen that initially the electronic excit-

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ation is essentially localized on the aromatic moiety. Since the olefinic moiety is much higher in energy in the excited singlet state manifold, two possible pathways exist for the isomerization of this moiety: (a) excited-state interaction between the aromatic and olefinic chromophores, allowing energy delocalization, and (b) intersystem crossing within the aromatic chromophore, with subsequent energy transfer to the olefinic part of the molecule. The second case would provide the following expression for the quantum yield of isomerization ($k^{A}_{i.s.c.}$ being the intersystem crossing rate constant of the aromatic moiety, b the fraction of olefinic triplets that isomerize) [equation (2)].

$$\phi_{\text{isom}} = \tau k^{A}_{\text{i.s.c.}}\, b \qquad (2)$$

Applying this equation to 1-phenylbut-2-ene[6] (using $k^{A}_{i.s.c.} = 1.6 \times 10^{7}$ s^{-1}, from toluene[7]) leads to values comparable to the experimental results. But, in the system under study here, this would lead to the values below those measured (using $k^{A}_{i.s.c.}$ from toluene and b calculated from the composition of the sensitized photostationary state): ϕ_{isom} 0.007 and 0.002 [from *E*- and *Z*-(IIa), respectively, see Table 1]. Pathway (b) alone clearly cannot account for the *E–Z* isomerization: the major portion must proceed through (a).

Significantly, 1-phenylbut-2-ene does not undergo di-π-methane rearrangement in the liquid phase[6] (although it does in the gas phase[8]).

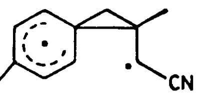
The rate constants for the singlet processes are given in Table 2 ($k_d = 1/\tau$). The increased deactivation of the singlet excited states of di-π-methane systems, compared to their isolated chromophores, has been ascribed by Zimmerman to a ' touching ' motion of the two π bonds.[9] In the case under study, besides a large increase from toluene[7] to *E*-(IIa), there is a further five-fold increase in k_d for *Z*-(IIa) (and a corresponding decrease for ϕ_f) * compared with *E*-(IIa).

TABLE 2

Rate constants for singlet processes of *E*- and *Z*-(IIa)

Compound	$10^{-9}k_d$/s^{-1}	$10^{-6}k_f$/s^{-1}	$10^{-7}k_{isom}$/s^{-1}	$10^{-7}k_{cp}$/s^{-1}
E-(IIa)	1.0	4.0	9.0	1.9
Z-(IIa)	5.0	4.5	74	6.0

The variation in the rate constants for cyclopropane formation parallels that of k_d. We believe that this parallelism may be explained by the similarity between the ' touching ' motion and the initial stages of the molecular reorganization leading to the proposed[10] diradical intermediate (IV) of the di-π-methane rearrangement. The increase in k_{isom} for *Z*-(IIa) suggests that this process may also be connected to the same kind of molecular motion mentioned above. Since cyclopropane formation is stereospecific, we think that (IV) is not directly involved here.



(IV)

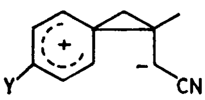
From the hypothesis of initial energy localization on the aromatic chromophore and emission therefrom (Table 1), k_f values for the *E*- and *Z*-isomers are expected to be invariant, and indeed they are observed to be quite similar to the value[7] for toluene (4.1 × 10^{6} s^{-1}).

Substituent Effects on Reaction (1).—The results obtained for a range of substituents Y in the Figure are summarized below (Table 3), together with absorption and emission data (cyclohexane solutions).

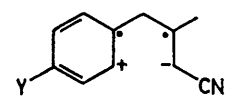
Contrary to the cases of Y = H (discussed above) and MeO, the triplet mechanism for *E–Z*-isomerization cannot be discounted for the other three substituents, and may be responsible for most of the observed ϕ_{isom}.

We proposed[1] the formation of a ' zwitterionic ' species as responsible for the deactivation of the excited singlet states of (I) and, indirectly, the observed di-π-methane rearrangement quantum yields of these molecules.

In the present case, (V) would be a representation of the analogous species.† Formation of both (IV) and (V) would be initially linked to the same reaction co-ordinate, *i.e.*, the ' touching ' motion. The electron-donating ability of the substituent Y facilitates this initial motion, but it will influence even more strongly the pathway leading to (V) [whereas (IV) should not be so sensitive to substitution].[11] In the case of *E*-(IIc), charge-transfer character on the early states would explain the red-shift in the fluorescence spectrum, compared to *p*-methoxytoluene,[12] which is absent in the absorption.



(V)



(VI)

On the energy surface towards (V), the molecule suffers demotion to the ground-state and, depending on its position, reverts to the starting isomer or proceeds to the *E–Z* isomerized configuration. This would provide a mechanism for singlet-state *E–Z* isomerization, mentioned in the previous section.

Support for this qualitative mechanistic model can be obtained from the data in Table 3, presented in modified form in Table 4 for purposes of comparison.

The ratio k_d^{o}/k_d expresses the effect of the ' touching ' deactivation. The ratio of isomerization and cyclopropane quantum yields, when both are singlet-state processes, will measure the competition between the two routes originating from the ' touching ' motion.

Solvent Effects.—Isomer *E*-(IIa) was irradiated in acetonitrile (AN), and the results [compared to cyclohexane (CH)] are $\phi_{isom}^{AN}/\phi_{isom}^{CH}$ 0.9; $\phi_{cr}^{AN}/\phi_{cp}^{CH} = 0.3$;

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* This decrease in ϕ_f between *E*- and *Z*-isomers was observed by us to be quite general for molecules related to 1-cyano-2-methyl-3-phenylpropene, either by ring substitution or methylation of the methylene bridging the aromatic and olefin moieties.

† A referee suggested another possible charged intermediate (VI).

TABLE 3

Substituent effects on reaction (1)

Compound	Substituent Y	ϕ_{isom}	ϕ_{cp} [a]	ϕ_f [b]	τ/ns [c]	k_d/s^{-1}	k_{isom}/s^{-1} [d]	k_{cp}/s^{-1}
E-(IIa)	H	0.090	0.019	0.004	1.0	1.0×10^9	9.0×10^7	1.9×10^7
E-(IIb)	CN	0.070	0.006 5	0.06	8.1	1.2×10^8		8.0×10^5
E-(IIc)	MeO	0.12	0.002 3	0.02	0.2 [e]	6.0×10^8	6.0×10^6	1.2×10^7
E-(IId) [f]	Cl	0.14	0.001 6	0.003	0.3 [g]	3.3×10^9		5.3×10^6
E-(IIe) [h]	Br	0.28						

[a] Cyclopropane formation not induced by triplet sensitization and essentially stereospecific. See Discussion section. [b] Emission and absorption spectra very similar to those of the corresponding *para*-substituted toluenes, except for fluorescence from *E*-(IIc), $\lambda_{max.}$ 315 nm (*p*-methoxytoluene,[14] $\lambda_{max.}$ 300 nm. [c] Lifetimes from single photon counting (see note *c* in Table 1) except for *E*-(IId). [d] *E–Z* isomerization considered as singlet process where values are given (see Discussion section). [e] Although this value was reproducibly obtained, we believe it lies at the limit of discrimination of the equipment used. [f] The product of Cl-bond cleavage and hydrogen capture from the solvent, (IIa), was also observed: $\phi_{(IIa)}$ 0.002. [g] Estimated from equation (1) and fluorescence data for *p*-chlorotoluene. [h] No di-π-methane rearrangement or fluorescence could be observed, but (IIa) was formed: $\phi_{(IIa)}$ 0.04.

$\phi_{isom}{}^{AN}/\phi_{cp}{}^{AN} = 13$. The effect of increased solvent polarity is to enhance the tendency to form (V) at the expense of (IV). This observation is entirely in accord with the foregoing and provides further evidence that deactivation leading to isomerization is a process which involves polar intermediates or transition states.

TABLE 4

Relative reactivities of compounds *E*-(II)

Substituent	Relative values[a] ϕ_{isom}	k_{cp}	$k_d{}^o/k_d$ [b]	ϕ_{isom}/ϕ_{cp}
H	1	1	0.03	4.7
CN	0.8	0.04	0.4	11
MeO	1.3	0.6	0.02	52
Cl	1.6	0.3	0.3	88
Br	3.1			

[a] Relative to *E*-(IIa). [b] $k_d{}^o$ is the total decay rate constant for the corresponding *para*-substituted toluene.

EXPERIMENTAL

General.—The details concerning instrumentation and solvent purification are given elsewhere.[1]

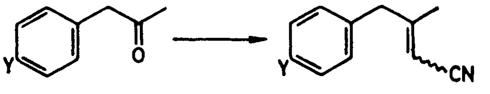
All quantum yields were measured at 254 nm, for <10% conversion. Solutions were degassed by three or four cycles of freeze–pump–thaw prior to irradiation (and fluorescence measurements). Actinometry was performed with cyclohexane solutions of 1,1-dicyano-2-methyl-3-phenylpropene;[1] the quantum yield values for *E*-(IIa) were checked with ferrioxalate actinometry[13] and the two values found to be in good agreement (within 10%). Toluene (ϕ 0.14[7]) and *p*-methoxytoluene (ϕ_f 0.26[12]) were used as fluorescence standards (cyclohexane solutions).

Product Analysis and Identification.—The irradiated mixtures, containing up to four compounds [the two isomers of (II) and the two isomers of (III)] were analysed by g.l.c. on 3% XE-60 columns (1/8 in × 5 or 20 ft).* For reliable analysis, conversions of up to 10% were necessary. OV-1 and TCEPE stationary phases achieved partial separation of the mixtures. The lack of thermal isomerizations during the g.l.c. analysis was confirmed by running irradiations to higher conversions, concentrating the mixtures, and analysing by ^{1}H n.m.r.

Product identities were established by (a) comparing retention times (on the three mentioned g.l.c. columns) with those of independently synthesised samples, (b) isolation from preparative scale irradiation by preparative g.l.c. (20% SE-30) and comparison of spectral data, and (c) coupled g.l.c.–mass spectroscopy.

Identification of (IIId) (only one isomer was observed) rested on the relative retention time [in all cases *E*-(III) was the first peak observed, followed by *Z*-(II)] and g.l.c.–m.s. experiments.

Synthesis of (II).—The reaction in Scheme 1 was used.



(II)

SCHEME 1 Reagents: $(EtO)_2P(O)CH_2CN$–$NaNH_2$–THF

The detailed procedures are given below. Diethyl cyanomethanephosphonate was prepared[14] by adding choroacetonitrile (0.2 mol), dropwise, to triethyl phosphite (0.22 mol) in a flask with stirrer and reflux condenser, at 135 °C.† The mixture was stirred overnight at that temperature, and for a further 2 h ‡ at 200 °C. Vacuum distillation yielded 81% of pure product (g.l.c. on 3% OV-1), δ 4.00—4.36 (4 H, dq, *J* 7.5 and 7 Hz), 3.05 (2 H, d, *J* 21 Hz), and 1.37 (6 H, *J* 7 Hz; coupled to the low-field signal).

Compounds (II) were prepared[15] by adding a solution of diethyl cyanomethanephosphonate (0.073 mol) in anhydrous THF (40 ml; distilled from sodium), dropwise, to sodamide (0.073 mol), at 0.5 °C, under nitrogen, with stirring. After addition, the mixture was allowed to reach room temperature and stirring was continued, with a slow stream of nitrogen passing through the flask, for 15 h. To the phosphonate anion thus formed, a solution of the appropriate arylacetone[1] (0.073 mol) in anhydrous THF (30 ml) was added dropwise. The mixture developed a gummy layer and, after stirring at room temperature for 5 h, water (200 ml) was added. After extraction with ethyl ether (3 × 150 ml), drying the extracts with $MgSO_4$ and evaporating the solvent, an oily residue was left. Except for (IIa) (where the products were isolated by distillation at 80 °C and 0.2 Torr), § the residues were bulb-to-bulb distilled under vacuum and the products isolated by preparative g.l.c. (20% SE-30). The required purity (>95% overall, >99% isomeric purity) was achieved by further preparative g.l.c. (20% SE-30 or 12% QF-1), and, finally, bulb-to-bulb distillation under vacuum.

The yields given (Table 5) refer to the reaction mixtures (g.l.c. on 3% OV-1, 1/8 in × 10 ft).

Synthesis of Compounds (III).—The steps in Scheme 2

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* 1 in = 0.025 4 m. 1 ft = 12 in.

† °C = K −273.15.

‡ 1 h = 60 min = 3 600 s.

§ 1 Torr ≈ 133.322 368 Pa.

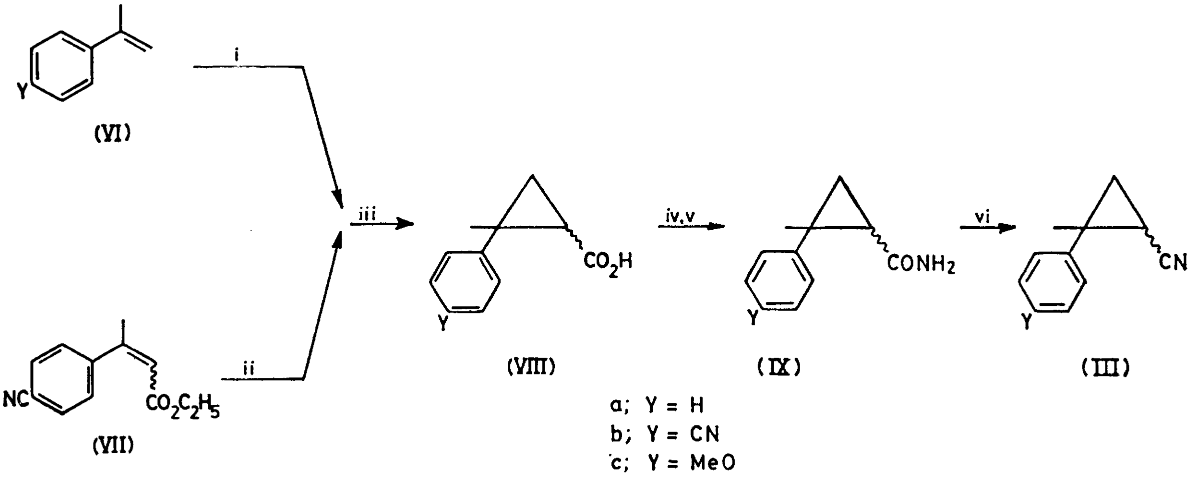
were used. The diazoacetate method failed to give (VIIIb). Attempts to cyclize (VIa) with $Me_2S{=}CH_2$ [16] or CH_2I_2–Cu–Zn [17] also failed. α-Methylstyrene (VIa) is available commercially; compound (VIc) was prepared in 56% yield from the corresponding acetophenone by the Wittig reaction.[18] Compound (VII) was synthesised from *p*-cyanoacetophenone by reaction with $(EtO)_2P(O)CHCO_2Et$ [19] in 78% yield.

TABLE 5

Synthesis of (II): yields and composition

Product	Yield (%)	Isomeric composition (%)	
		Z	*E*
(IIa)	50	26	74
(IIb)	50	33	67
(IIc)	80	30	70
(IId)	76	31	69
(IIe)	61	30	70

^{1}H n.m.r. ($CDCl_3$): (VIc), δ 6.75—7.60 (4 H, m), 5.29sbr (1 H, s), 4.99br (1 H, s), 3.73 (3 H, s), and 2.11 (3 H, s); (VII), δ 7.5—7.85 (4 H, m), 6.17br and 5.99br (1 H, 2 × s, 80 : 20 ratio), 4.4—3.9 (2 H, 2 superimposed q, *J* 7 Hz), 2.56br and 2.18br (3 H, 2 × s, 78 : 22 ratio), and 1.45—0.95 (3 H, 2 × t, *J* 7 Hz).



SCHEME 2 Reagents: i, N_2CHCO_2Et; ii, $(Me)_2S(O){=}CH_2$; iii, NaOH; iv, $SOCl_2$; v, NH_4OH; vi, P_2O_5–Et_3N

The detailed procedure used to obtain (VIIIa and c) was as follows.[20] Ethyl diazoacetate (0.13 mol) was slowly added (2 h) to (VI) (0.13 mol) at 150 °C, with stirring, and the temperature kept constant during the addition. (The progress of the reaction can be followed by the production of N_2 bubbles). After stirring at 150 °C for a further 1.5 h, the mixture was allowed to cool and KOH (0.14 mol) in 95% ethanol (100 ml) was added. Following reflux for 1 h, ethanol was distilled off and water (100 ml) added. The water layer was separated and the organic layer washed with water. After washing the combined water extracts with ethyl ether (50 ml), they were acidified with 10% HCl (100 ml) and extracted with ether (3 × 100 ml). After drying ($MgSO_4$), the solvent was evaporated, leaving an oily residue. Yields of crude acids (used on next step): (VIIIa), 65%; (VIIIc), 44%. ^{1}H N.m.r. ($CDCl_3$): (VIIIa), δ 11.5 (1 H, s), 7.25 (5 H, s), 2.2 (6 H, a complex of peaks, with a prominent singlet at δ 1.55); (VIIIc), 11.52 (1 H, s), 6.7—6.35 (4 H, m), 3.7 (3 H, s), and 2.1—1.2 (6 H m). The peaks at δ 11.5 and 11.52 disappear after shaking with D_2O.

The procedure to obtain compound (VIIIb) was as follows.[16] A dispersion of sodium hydride in oil (at 60%, containing 0.042 mol NaH) was washed with dry pentane (3 × 10 ml) and, after decanting the last portion, the flask was evacuated and nitrogen admitted. Trimethylsulphoxonium iodide (0.042 mol) was added and, then, dimethyl sulphoxide (DMSO) (25 ml) (distilled from CaH_2) added dropwise with a syringe, while stirring (all operations at room temperature). After the foaming stopped, a solution of compound (VII) (0.039 mol) in dry DMSO (30 ml) was added with a syringe. After stirring the reddish mixture for 1.5 h, ice–water was added. The mixture was extracted with ethyl ether (3 × 100 ml), the ether extracts washed with brine, and the solvent evaporated. The resulting oil was stirred at room temperature with a 5% solution of NaOH in methanol (200 ml) for 3.5 h. The methanol was stripped off, water (300 ml) added, the mixture extracted with ether (100 ml), and the water layer acidified with HCl. Extraction of the acidified aqueous mixture with chloroform (3 × 100 ml) afforded, after drying ($MgSO_4$) and evaporating the solvent, a thick yellowish oil [crude (VIIIb)] in 40% yield. This was used in the next steps.

The last two steps were performed as follows.[21] Crude acid (VIII) (1.0 g), thionyl chloride (0.7 ml), chloroform (4 ml), and dimethylformamide (6 drops, distilled from molecular sieves), were refluxed for 15 min, left at room temperature for 10 min, cooled to −5 °C, and poured into concentrated NH_4OH (130 ml) at −10 °C. The mixture was stirred at −10 °C for 3 min and at room temperature for a further 10 min. The two layers were separated, the aqueous layer extracted with chloroform (3 × 50 ml), the combined chloroform layers washed with brine, dried over $MgSO_4$, filtered, and the solvent evaporated to give a nearly quantitative yield of amide (IX). In the case of (IXb) the final step used the crude amide. Compounds (IXa and c) were purified by sublimation under vacuum (150 °C and 0.004 Torr).

^{1}H N.m.r.: (IXa) ([$^2H_6$]DMSO), δ 7.2 br (5 H, s), 5.7vbr and 5.4vbr (2 H, 2 × s), 2.2—1.0 (6 H, complex of peaks with two prominent s in 72 : 28 ratio at δ 1.31 and 1.19); (IXc) ($CDCl_3$) δ 6.7—7.3 (4 H, m), 5.35vbr and 5.7vbr (2 H, 2 × s), 3.76 (3 H, s), 1.9—1.2 (6 H, complex of peaks with two prominent singlets at δ 1.41 and 1.50 in 40 : 60 ratio).

Compound (IX) (0.3 g) in chloroform (25 ml, distilled from P_2O_5) was added to P_2O_5 (1.5 g) covered by dry sand (10 g), in a dry flask. Triethylamine (5 ml, distilled from KOH) was added dropwise. Reflux with stirring for 2 h was followed by decantation of the chloroform layer which was washed with 1N-HCl, saturated $NaHCO_3$ solution, and brine. After drying over $MgSO_4$, filtering, and evaporating the solvent, an oily residue was left. The pure isomers of (III) were then isolated by column chromatography (SiO_2–hexane–chloroform) in the case of (IIIa), preparative t.l.c. (SiO_2; four elutions with benzene) for (IIIb), or preparative g.l.c. (14% XE-60, 1/4 in × 5 ft, 220 °C) with (IIIc).

Spectral Data for (II) *and* (III).—All ^1H n.m.r. spectra were measured for $CDCl_3$ solutions; chemical shifts are on the δ scale; internal Me_4Si was the reference. The spectra of all new compounds were consistent with the structures assigned.

In the spectra of (II) allylic coupling between the olefinic and allylic protons (*J* 1—2 Hz) was demonstrated by decoupling. For some substituents (MeO and CN) an AA′BB′ pattern was seen for the aromatic protons.

TABLE 6

U.v. data

Compound	$\lambda_{max.}$/nm (ϵ)
Z-(IIa)	254sh(380), 261(350), 263(300), 266(240), 270(220)
E-(IIa)	254sh(260), 261(270), 263sh(220), 266(210), 270(140)
E-(IIb)	261(750), 268(730), 274(600), 280(450)
E-(IIc)	279(2 000), 286(1 800)
E-(IId)	262(470), 269(490), 278(400)
E-(IIe)	263(510), 270(480), 279(350)
E-(IIIa)	255(250), 261(290), 267(250)

The cyclopropane ring protons of (III) form a complex ABC pattern with the methyl singlet protruding. In the case of *E*-(IIIa), addition of $Eu(fod)_3$ shift reagent transformed the ABC pattern into a ABX pattern; the X component was a doublet of doublets and the ordering (from low-field side) became: X, methyl, AB; the integration then gave 1 H, 3 H, 2 H.

U.v. spectra were measured for cyclohexane solutions. Features are given by their wavelength (in nm) followed by the extinction coefficient (ε). Sh identifies a shoulder; all the other features are peaks.

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