Transmission of Polar Effects. Part 21.[1] Alkaline Hydrolysis of the 2'- and 4'-substituted 2-Methoxycarbonyldiphenylacetylenes and (*Z*)-2'- and -4'-Substituted 2-Methoxycarbonylstilbenes and the Ionisation and Esterification, with Diazodiphenylmethane of the Acids of the Latter Series

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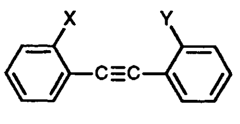
The rate coefficients for the alkaline hydrolysis of a series of 2'- and 4'-substituted 2-methoxycarbonyldiphenylacetylenes and (*Z*)-2-methoxycarbonylstilbenes have been determined in 70% (v/v) dimethyl sulphoxide–water at both 30.0 and 50.0 °C and at 24.0, 30.0, 40.0, and 50.0 °C, respectively. The $\mathrm{p}K_\mathrm{a}$ values of (*Z*)-2'- and -4'-substituted 2-carboxystilbenes have been measured in 80% (w/w) 2-methoxyethanol–water at 25 °C. The rate coefficients for the esterification of the corresponding acids with diazodiphenylmethane have been measured at 30.0 °C. For the diphenylacetylene system, normal substituent effects are observed from both the 2'- and 4'-position. A transmission coefficient for polar effects of *ca.* 0.2 has been calculated for *both* positions. The evidence, including the carbonyl stretching frequencies of the esters, indicates an s-*trans* conformer for the 2'-substituted 2-methoxycarbonyldiphenylacetylenes. For the (*Z*)-stilbene system, normal substituent effects are observed from both the 2'- and 4'-position. Transmission coefficients for polar effects, with regard to *both* the 2'- or 4'-position and the reaction studied, vary between 0.2 and 0.7. This appears to arise from the conformers available to the (*Z*)-2'- and -4'-substituted 2-carboxystilbenes.

In previous studies in this series,[1–7] it has been possible to demonstrate unequivocably the transmission of polar effects by an electrostatic field path. Furthermore, a number of these studies[1,3–6] demonstrated the reversal of dipolar substituent effects when the correct design conditions are present in a molecular model. It is now possible to use this knowledge to investigate the conformation of a suitable model and to use our present understanding of substituent effects in a diagnostic manner. Such a system is diphenylacetylene. Diphenylacetylene is a linear, coplanar molecule; with a small barrier to rotation of <2 kcal mol^{-1},[8,9,†] *both* in the solid state and in solution. For a 2,2'-disubstituted system, two coplanar forms can exist, as long as the substituents X and Y are not very 'bulky'. These are the s-*cis* (1) and s-*trans* (2) conformers. in conformer (1), reversed dipolar substituent effects would be expected, while in conformer (2) normal substituent effects are expected. Only one isomer can occur for a 2,4'-substituted system, *i.e.* compound (3). In the latter system, if the substituent is X and the reactive site is Y, normal substituent effects would be expected. On the other hand, (*Z*)-stilbene is *not* coplanar, but has a 'propeller-shaped' conformation in which the phenyl rings are rotated about 30° out of plane.[10] Furthermore, substitution of the type described above results in a more complex situation. The conformers possible can be 'idealised,' as shown below as the s-*cis-cis* (4), s-*cis-trans* (5), s-*trans-cis* (6), and s-*trans-trans* (7) conformers. However, a degree of twisting will occur. The result will be partial deconjugation of both the phenyl and ethylenic groups, as well as both substituents (if applicable).



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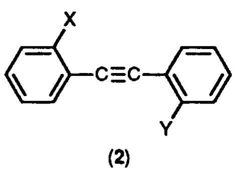

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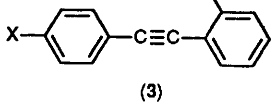

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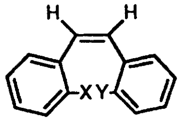

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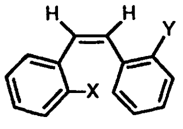

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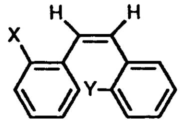

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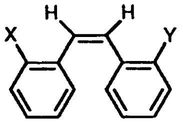

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In the present study we have prepared novel systems to test the reactivity considerations above. The systems studied are the 2'- or 4'-substituted 2-methoxycarbonyldiphenylacetylenes and *cis*-2-methoxycarbonylstilbenes, as well as the corresponding acids of the latter system. The reactivity of the systems has been assessed by a study of the alkaline hydrolysis of the methyl esters and of the ionisation and esterification of the acids with diazodiphenylmethane (DDM).

Results and Discussion

Alkaline Hydrolysis of the 2'- and 4'-Substituted 2-Methoxycarbonyldiphenylacetylenes.—The alkaline hydrolysis of these methyl esters has been stuied in 70% (v/v) dimethyl sulphoxide

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† 1 cal = 4.184 J.

Table 1. Rate coefficients (k_2) for the alkaline hydrolysis of 2′- and 4′-substituted 2-methoxycarbonyldiphenylacetylenes in 70% (v/v) DMSO–water.[a]

Substituent[b]	k_2/dm^3 mol^{-1} min^{-1} At 30.0 °C	k_2/dm^3 mol^{-1} min^{-1} At 50.0 °C
H	9.78	37.6
2′-Br	12.6	48.2
2′-Cl	13.6	50.5
2′-NO$_2$	19.2	74.4
2′-Me	8.29	32.5
2′-OMe	8.99	34.9
4′-Br	12.3	49.0
4′-Cl	14.8	56.8
4′-Me	9.63	35.4
4′-OMe	7.33	26.9

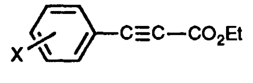
[a] Rate coefficients are reproducible to within ±3%. [b] The alkaline hydrolysis of the 4′-NO$_2$ ester could not be measured (see the text).

Table 2. Activation of parameters at 30.0 °C for the alkaline hydrolysis of 2′- and 4′-substituted 2-carboxymethyldiphenylacetylenes in 70% (v/v) dimethyl sulphoxide–water.[a]

Substituent	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}
H	12.3	−13
2′-Br	12.2	−13
2′-Cl	11.9	−14
2′-NO$_2$	12.3	−12
2′-Me	12.4	−13
2′-OMe	12.4	−13
4′-Br	12.6	−12
4′-Cl	12.2	−13
4′-Me	11.8	−15
4′-OMe	11.8	−15

[a] Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are considered accurate to within ±300 cal mol^{-1} and ±2 cal mol^{-1} K^{-1}, respectively.

(DMSO)–water at 30.0 and 50.0 °C, as shown in Table 1. The activation parameters are shown in Table 2. The effects of substitution at the 4′-position are quite normal, as would be expected, and are correlated by the Hammett equation, as shown in Table 3. The correlations are not very successful, but are better using σ[11] than σ^n.[12] Thus, through-resonance effects are present in the coplanar and conjugated diphenylacetylene system. The transmission of polar effects in this system can be assessed. Thus ρ/ρ_0 can be calculated to be *ca.* 0.20, using data from the alkaline hydrolysis of methyl benzoates under similar conditions, *i.e.* ρ_0 2.40 for 65% (v/v) DMSO–water at 30 °C,[13] as the reference reaction. This transmission factor can be compared with a value of 0.13 calculated for the system using the transmission coefficients tabulated by Bowden[14] or, more realistically, with 0.21, being the product of transmission factors obtained for the alkaline hydrolysis of ethyl phenylpropiolates[15] (**8**) and (*Z*)-cinnamates[16] (**9**). Thus, the transmission appears both normal and reasonable. The effects of substitution at the 2′-position are also normal and are *not* reversed, *i.e.* the electron-withdrawing substituents show their normal accelerating rate effect in alkaline hydrolysis. Further, the ratios of the effect of identical substituents at the 2′- and 4′-position are in the range 1.2–0.9, *i.e.* close to unity. In an earlier study,[2] Bowden and Parkin suggested that *para*-σ-values could be used successfully in the correlation of *ortho*-substituent effects, when steric effects were either absent or constant. Furthermore, if the site of substitution was 'distant,' the reaction constants for both *ortho*- and *meta*/*para*-substitution would tend to become equal. In Table 3, the 2′-substituent effects for alkaline hydrolysis have been correlated successfuly with σ and σ^n. The more successful correlations, using σ-values, give ρ-values identical within the range of the uncertainties for both the 2′- and 4′-series. All these considerations indicate that the s-*trans*-conformer (**2**) is the stable species. This conformer will give normal substituent effects for 2′-substituents and will have a similar transmissive cavity for both 2′- and 4′-substituents. Examination of models of these two conformers (**1**) and (**2**) indicates the absence of significant steric effects, even between the 2′- and 2-substituents in conformer (**1**). However, model calculations do indicate a small, but significant, overall repulsive electrostatic effect between a 2′-bromo and 2-methoxycarbonyl group in conformer (**1**). The small rate differences observed in the alkaline hydrolysis also result in small differences in activation parameters, as shown in Table 2. These changes are often within the uncertainties in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. However, significant steric effects would have been expected to result in much larger changes for 2′-substitution and thus such effects can be confirmed to be absent.



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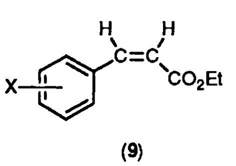

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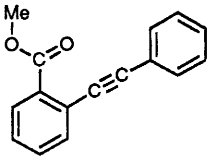
Carbonyl Stretching Frequencies of the 2-Methoxycarbonyldiphenylacetylenes.—The very moderate 'lateral' steric requirements of the acetylene group[17] as an *ortho*-substituent for methyl benzoate, confirmed by examination of molecular models, suggests a coplanar arrangement of the diphenylacetylene *and* methoxycarbonyl groups. However, the methoxycarbonyl group could give rise to an s-*cis* (**10**) or s-*trans* (**11**) conformation. Brooks *et al.*[18] demonstrated that a number of methyl *ortho*-substituted benzoates have two carbonyl stretching absorptions, corresponding to two conformers of the types (**10**) and (**11**). The *ortho*-substituents studied previously were the halogeno and methoxy groups. These workers assigned the absorptions close to 1 730 cm^{-1} to the isomer corresponding to (**11**) and those close to 1 740 cm^{-1} to isomers such as (**10**).[18] The carbonyl stretching frequencies of the 2′- and 4′-substituted 2-methoxycarbonyldiphenylacetylenes are shown in Table 4. Two absorptions are noted for *all* esters, *i.e.* both the 2′- and 4′-substituted. Thus, these absorptions must relate to the conformers (**10**) and (**11**) and cannot correspond to conformers (**1**) and (**2**), as then the twin absorptions would only occur for 2′-substituted esters. The absorption at *ca.* 1 735 cm^{-1} is tentatively assigned to conformer (**10**), while that at *ca.* 1 720 cm^{-1} is assigned to conformer (**11**). The conformers would have the same type of environment, both stereochemical and electrostatic, as the *ortho*-halogeno or -methoxy esters. Hammett σ-values indicate that the ethynyl (–C≡C–H) group is electron withdrawing.[19] The dipolar character of the substituent, regarding the benzene system, is qualitatively of the same type as the halogeno groups.



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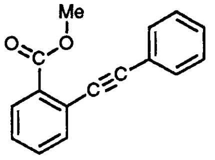

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Alkaline Hydrolysis of the (Z)-2′- and 4′-Substituted 2-Methoxycarbonylstilbenes.—The alkaline hydrolysis of these methyl esters has been studied in 70% (v/v) DMSO–water at

Table 3. Hammett reaction constants, ρ, for the reactivity of the 2′- and 4′-substituted 2-methoxycarbonyldiphenylacetylenes and (*Z*)-2′- and -4′-substituted 2-methoxycarbonyl- and 2-carboxy-stilbenes.[a]

		ρ	$\log k_0$	*s*	*r*	*N*
(i) Alkaline hydrolysis						
2′-Substituted diphenylacetylenes at 30 °C	(a)	0.393	0.995	0.035	0.984	6
	(b)	0.353	1.016	0.040	0.975	6
4′-Substituted diphenylacetylenes at 30 °C	(a)	0.475	1.018	0.104	0.935	5
	(b)	0.528	0.991	0.174	0.869	5
2′-Substituted (*Z*)-stilbenes at 30 °C	(a)	0.495	0.613	0.124	0.917	6
	(b)	0.581	0.584	0.163	0.899	5
4′-Substituted (*Z*)-stilbenes at 30 °C	(a)	0.379	0.613	0.098	0.913	5
	(b)	0.482	0.588	0.070	0.970	5
(ii) Ionisation						
2′-Substituted (*Z*)-stilbenes	(a)	0.789	6.50	0.289	0.838	5
	(b)	0.954	6.55	0.313	0.869	5
4′-Substituted (*Z*)-stilbenes	(a)	0.330	6.59	0.080	0.919	5
	(b)	0.423	6.61	0.040	0.985	5
(iii) Esterification with DDM						
2′-Substituted (*Z*)-stilbenes	(a)	0.799	−0.227	0.213	0.908	5
	(b)	0.942	−0.275	0.272	0.894	5
4′-Substituted (*Z*)-stilbenes	(a)	0.672	−0.204	0.153	0.930	5
	(b)	0.851	−0.247	0.089	0.984	5

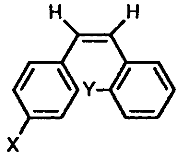
[a] The value *s* is the standard deviation, *r* the correlation coefficient, and *N* the number of substituents studied. Correlation (a) with σ and (b) with σ^n.

Table 4. Carbonyl stretching frequencies (ν_{max}) of 2′- and 4′-substituted 2-methoxycarbonyldiphenylacetylenes in tetrachloromethane.

Substituent	ν_{max}/cm^{-1}	$\varepsilon_1/\varepsilon_2$[a]
H	1 735.5, 1 719.5	1.2
2′-Br	1 735, 1 721	1.2
2′-Cl	1 735, 1 721	1.1
2′-NO_2	1 733, 1 723	1.6
2′-Me	1 737, 1 720	1.4
2′-OMe	1 735, 1 718.5	1.2
4′-Br	1 734, 1 720.5	1.5
4′-Cl	1 734, 1 720	1.4
4′-NO_2	1 731, 1 725	1.7
4′-Me	1 736, 1 719	1.2
4′-OMe	1 735, 1 717.5	1.3

[a] Relative intensities (higher ν/lower ν).

24.0, 30.0, 40.0, and 50.0 °C, as shown in Table 5. The activation parameters are shown in Table 6. The trends in the substituent effects parallel those observed for the diphenylacetylene system. The effects of substitution in the 4′-substituted series are correlated by the Hammett equation (see Table 3) and, for this system, better by σ^n than σ. The transmission coefficient can be calculated as before to be *ca.* 0.20. This can be compared with a value of 0.18 calculated using the transmission coefficients tabulated by Bowden.[14] The effects of 2′-substitution, which are normal and *not* reversed, are very similar to those of the same substituent at the 4′-position. Using *para*-σ-values, the reaction constants obtained for substitution at the 2′-position are similar to those for the 4′-position, although the correlations are only moderately successful. It is very difficult to assign conformations with any confidence to these esters. Even the 4′-substituted series can exist as two conformers, which are 'idealised' below as *s-cis* (**12**) and *s-trans* (**13**). The activation parameters, as shown in Table 6, show small changes and are, with one exception, within the uncertainties. Again no evidence for significant steric effects in these reactions is observed for the 2′-substituted series.



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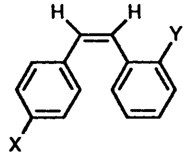

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Ionisation and Esterification, with DDM, of the (Z)-2′- *and* 4′-*Substituted* 2-*Carboxystilbenes*.—The pK_a values of the acids in 80% (w/w) 2-methoxyethanol–water at 25 °C are shown in Table 7. The pK_a value of the parent acid is between that of benzoic and *ortho*-phenylbenzoic acid, *i.e.* 6.68[20] and 6.47,[7] respectively, as would be expected. The Hammett correlations for the 4′-substituted series are shown in Table 3 and that using σ^n is good. This allows calculation of the transmission coefficient, ρ/ρ_0, as 0.25 for this system, taking ρ_0 for benzoic acids under the same conditions as being 1.66.[21] This result for the transmission coefficient compares closely with that for the alkaline hydrolysis reaction for this system. However, the results for 2′-substitution are quite unlike those for the alkaline hydrolysis reaction of the (*Z*)-stilbenes and the diphenylacetylenes. With the exception of the 2′-Me compound, the ΔpK_a values are very much larger for 2′- than for 4′-substitution. Further, the Hammett correlation for the 2′-substituents, although poor, indicates a ρ value *ca.* twice that for 4′-substitution. This results in a transmission coefficient, calculated as before, of 0.68. This type of behaviour is shown by *both* the 2′- and 4′-substituents in their esterification reaction with DDM. The Hammett correlation for the 4′-substituents is shown in Table 3 and is good with σ^n. The transmission coefficient, ρ/ρ_0, can be calculated as 0.72, taking ρ_0 for benzoic acids under the same conditions as being 1.18.[22] The correlation for 2′-substitution is again poor, but gives a transmission coefficient of *ca.* 0.7.

The results for the (*Z*)-stilbenes are obviously complex, but appear to be consistent. Thus, the unusually small acid-strengthening, noted in Table 7, for the 2′-Me group in the ionisation is reproduced in the esterification reaction. It would appear that the very small energy barriers expected[23] between the 'true' conformers, represented by conformers (**5**), (**6**), and (**7**), and by conformers (**12**) and (**13**), allow switches to be made to take advantage of higher conformer reactivity. This would

Table 5. Rate coefficients (k_2) for the alkaline hydrolysis of (Z)-2′- and -4′-substituted 2-methoxycarbonylstilbenes in 70% (v/v) DMSO–water.[a]

	k_2/dm^3 mol^{-1} min^{-1}			
Substituent	At 24.0 °C	At 30.0 °C	At 40.0 °C	At 50.0 °C
H	2.10	3.54	7.50	15.2
2′-Br	3.06	4.97	10.5	21.6
2′-Cl	3.95	6.10	12.1	22.3
2′-Me	2.16	3.66	8.85[b]	16.2[c]
2′-OMe	1.93	3.03	6.37	12.5
4′-Br	3.32	5.21	10.6	21.0
4′-Cl	3.30	5.24	10.1	20.8
4′-Me	2.09	3.48	7.18	14.4
4′-OMe	2.12	3.51	6.77	14.1

[a] Rate coefficients are reproducible to within ±3%. [b] At 42.0 °C. [c] At 51.0 °C

Table 6. Activation parameters at 30.0 °C for the alkaline hydrolysis of (Z)-2′- and -4′-substituted 2-methoxycarbonylstilbene in 70% (v/v) DMSO–water.[a]

Substituent	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal mol^{-1} K^{-1}
H	13.9	−10
2′-Br	13.7	−10
2′-Cl	12.1	−15
2′-Me	13.6	−11
2′-OMe	13.2	−13
4′-Br	12.0	−13
4′-Cl	12.8	−13
4′-Me	13.5	−12
4′-OMe	13.1	−13

[a] Values of $\Delta H^‡$ and $\Delta S^‡$ are considered accurate to within ±300 cal mol^{-1} and ±2 cal mol^{-1} K^{-1}, respectively.

Table 7. pK_a Values in 80% (w/w) 2-methoxyethanol–water at 25 °C and rate coefficients (k_2) for the esterification (with DDM in 2-methoxyethanol at 30.0 °C) of (Z)-2′- or -4′-substituted 2-carboxystilbenes.[a]

Substituent	pK_a	k_2/dm^3 mol^{-1} min^{-1}
H	6.62	0.504
2′-Br	6.17	1.15
2′-Cl	6.43	0.752
2′-Me	6.58	0.512
2′-OMe	6.70	0.340
4′-Br	6.48	0.956
4′-Cl	6.52	0.946
4′-Me	6.67	0.456
4′-OMe	6.64	0.474

[a] The measurements are the mean of at least two determinations. The pK_a values are reproducible to within ±0.01 units and rate coefficients to within ±3%.

result in changes in transmissive capacity which would vary between conformers (**5**), (**6**), and (**7**), and between (**12**) and (**13**). It is difficult even to speculate on the conformers employed in each type of reactivity. However, on the basis of electrostatic transmission, it would be expected[14] that transmission would be in the order (**5**) ~ (**6**) > (**7**) and (**12**) > (**13**). The relative success of those correlations using σ^n for 4′-substitution in the (Z)-stilbene system confirms the partial deconjugation present in such systems.

Experimental

Materials.—The 2-methoxycarbonyldiphenylacetylenes and (Z)-2-methoxycarbonylstilbenes, as well as the corresponding acids of the latter system, were prepared by the following sequence. The cinnamic acids were prepared from the corresponding benzaldehydes by means of the Perkin reaction. The cinnamic acids were converted into the styrenes by decarboxylation using Cu–quinoline. Bromine was added to the latter product and the product was dehydrobrominated with sodium amide in liquid ammonia to give the phenylacetylene. The copper(I) phenylacetylides were coupled with methyl 2-iodobenzoate in pyridine to give the 2-methoxycarbonyldiphenylacetylenes. The latter were catalytically reduced and then hydrolysed to give the (Z)-2-methoxycarbonyl- and -carboxystilbenes, respectively.

2-*Methoxycarbonyldiphenylacetylene.*—This *ester* was prepared by the method of Castro and Stephens,[24] from methyl 2-iodobenzoate and copper(I) phenylacetylide.

2′-*Bromo-, -Chloro-, -Nitro-, -Methoxy-, and -Methyl-, and* 4′-*Bromo-, -Chloro-, -Nitro-, -Methoxy-, and -Methyl-*2-*methoxycarbonyldiphenylacetylenes.*—These *esters* were synthesized by the above method using the corresponding copper(I) 2- or 4-substituted phenylacetylide.

(Z)-2-*Methoxycarbonylstilbene.*—A solution of the 2-methoxycarbonyldiphenylacetylene (2.1 g, 8.9 mmol) in pyridine (100 cm^3) was stirred at room temperature in the presence of 5% palladium on barium sulphate (1.2 g) under hydrogen at atmospheric pressure. After 1 mol equiv. of hydrogen had been absorbed, the reaction mixture was filtered through Hyflo-supercel. The filter pad was then washed with ethyl acetate. The filtrate and washings were evaporated to give a viscous oil, which was dissolved in ethyl acetate. The solution was washed successively with hydrochloric acid (1 mol dm^{-3}) and water, dried (MgSO$_4$), and filtered. The residue, after evaporation, was dissolved in methanol and treated with activated carbon (0.1 g), while hot. After filtration, the hot solution was stored and the title ester (1.2 g, 57%) was obtained as a crystalline solid.

(Z)-2′-*Bromo-, -Chloro-, -Methoxy-, and -Methyl-, and -*4′-*Bromo-, -Chloro-, -Methoxy-, and -Methyl-*2-*methoxycarbonylstilbenes.*—These *esters* were synthesized by the above method.

(Z)-2-*Carboxystilbene.*—2-Methoxycarbonyldiphenylacetylene (1.2 g, 5 mmol) was added slowly to a solution of potassium hydroxide (0.5 g, 0.009 mol) in 95% aq. ethanol (100 cm^3), with care. After the initial reaction had subsided, the solution was refluxed for 1 h. The solution was then evaporated and the residue was dissolved in water (100 cm^3). The aqueous solution was extracted with diethyl ether (2 × 75 ml), before neutralisation with hydrochloric acid (18%) while being cooled in an ice-bath. The aqueous solution was extracted with diethyl ether. The extract was dried (MgSO$_4$), filtered, and then evaporated. The acid was then dissolved in aq. sodium carbonate, precipitated with aq. hydrochloric acid, and extracted again with diethyl ether. The dried extract was evaporated to give the crude title acid, which was recrystallised from aqueous ethanol as a crystalline solid (1.0 g, 89%).

(Z)-2′-*Bromo-, -Chloro-, -Methoxy-, and -Methyl-, and -*4′-*Bromo-, -Chloro-, -Methoxy-, and -Methyl-*2-*carboxystilbene.*—The *acids* were synthesized by the above method.

The m.p.s, elemental analyses, and recrystallisation solvents of the *acids* and *esters* are shown in Table 8.

Attempted Preparation of the 4′- *and* 2′-*Substituted* 2-*Carboxydiphenylacetylenes.*—These *esters*, with the exception of the

Table 8. Physical constants of the 2′- and 4′-substituted 2-methoxycarbonyldiphenylacetylenes and (*Z*)-2′- and -4′-substituted 2- methoxycarbonylstilbenes, as well as the corresponding acids.

Substituent	M.p./ °C	Formula	Found (%)			Required (%)			Recrystallisation solvent
			C	H	Other	C	H	Other	
2-Methoxycarbonyldiphenylacetylenes									
H	128/0.2 mmHg[a]	$C_{16}H_{12}O_2$	81.1	5.1		81.3	5.1		
2′-Br	69/0.05 mmHg[a]	$C_{16}H_{11}BrO_2$	60.6	3.5	25.7 (Br)	61.0	3.5	25.4 (Br)	
2′-Cl	29–30	$C_{16}H_{11}ClO_2$	71.0	4.0	13.0 (Cl)	71.4	4.1	13.1 (Cl)	light petroleum (b.p. 60–80 °C)–benzene
2′-NO$_2$	91–92	$C_{16}H_{11}NO_4$	68.3	3.8	4.9 (N)	68.3	3.9	5.0 (N)	MeOH
2′-Me	71–72/0.2 mmHg[a]	$C_{17}H_{14}O_2$	81.1	5.6		81.6	5.6		
2′-OMe	63–65	$C_{17}H_{14}O_3$	76.6	5.3		76.7	5.3		light petroleum (b.p. 60–80 °C)–benzene
4′-Br	66–68	$C_{16}H_{11}BrO_2$	60.5	3.4	25.5 (Br)	61.0	3.5	25.4 (Br)	light petroleum (b.p. 60–80 °C)–EtOH
4′-Cl	52–52.5	$C_{16}H_{11}ClO_2$	70.7	4.1	13.2 (Cl)	71.0	4.1	13.1 (Cl)	light petroleum (b.p. 60–80 °C)–benzene
4′-NO$_2$	99–101	$C_{16}H_{11}NO_4$	68.4	4.0	4.9 (N)	68.3	3.9	5.0 (N)	light petroleum (b.p. 30–40 °C)–EtOH
4′-Me	20–22	$C_{17}H_{14}O_2$	81.6	5.5		81.6	5.6		light petroleum (b.p. 40–60 °C)–EtOH
4′-OMe	67–69	$C_{17}H_{14}O_3$	76.6	5.3		76.7	5.3		light petroleum (b.p. 40–60 °C)–benzene
(*Z*)-2-Methoxycarbonylstilbenes									
H	72–73[b]	$C_{16}H_{14}O_2$	81.0	6.2		80.7	5.9		MeOH
2′-Br	61–62	$C_{16}H_{13}BrO_2$	59.9	4.0	24.5 (Br)	60.6	4.1	25.5 (Br)	light petroleum (b.p. 60–80 °C)–benzene
2′-Cl	53–55	$C_{16}H_{13}ClO_2$	70.7	5.0	13.1 (Cl)	70.5	4.8	13.0 (Cl)	light petroleum (b.p. 60–80 °C)–benzene
2′-Me	42–43	$C_{17}H_{16}O_2$	76.1	6.5		76.2	6.4		MeOH
2′-OMe	47–49	$C_{17}H_{16}O_3$	76.5	6.2		76.1	6.0		light petroleum (b.p. 60–80 °C)–benzene
4′-Br	58–60	$C_{16}H_{13}BrO_2$	60.9	4.3	25.2 (Br)	60.6	4.1	25.2 (Br)	light petroleum (b.p. 60–80 °C)–benzene
4′-Cl	60–62	$C_{16}H_{13}ClO_2$	70.0	4.8	12.9 (Cl)	70.5	4.8	13.0 (Cl)	light petroleum (b.p. 60–80 °C)–benzene
4′-Me	18–20	$C_{17}H_{16}O_2$	76.6	6.2		76.2	6.4		MeOH
4′-OMe	39–40	$C_{17}H_{16}O_3$	75.7	6.3		76.1	6.0		light petroleum (b.p. 60–80 °C)–benzene
(*Z*)-2-Carboxystilbenes									
H	143–145[c]	$C_{15}H_{12}O_2$	80.3	5.5		80.3	5.4		aq. EtOH
2′-Br	149–151	$C_{15}H_{11}BrO_2$	59.0	3.2	26.3 (Br)	59.4	3.7	26.4 (Br)	EtOH
2′-Cl	141–142	$C_{15}H_{11}ClO_2$	69.6	4.4	13.1 (Cl)	69.6	4.3	13.7 (Cl)	EtOH
2′-Me	138–139	$C_{16}H_{14}O_2$	80.4	5.9		80.7	5.9		aq. EtOH
2′-OMe	146–148	$C_{16}H_{14}O_3$	75.5	5.9		75.6	5.6		aq. EtOH
4′-Br	162–163	$C_{15}H_{11}BrO_2$	59.6	3.8	26.3 (Br)	59.4	3.7	26.4 (Br)	benzene–acetone
4′-Cl	149–151	$C_{15}H_{11}ClO_2$	70.2	4.6	13.0 (Cl)	69.6	4.3	13.7 (Cl)	benzene–acetone
4′-Me	153–155	$C_{16}H_{14}O_2$	80.1	5.9		80.7	5.9		benzene–acetone
4′-OMe	120–122	$C_{16}H_{14}O_3$	75.3	5.7		75.6	5.6		benzene–acetone

[a] B.p. [b] Lit.,[25] m.p. 74–75 °C. [c] Lit.,[25] m.p. 145–146.5 °C.

4′-nitro ester (see later), gave stable products on alkaline hydrolysis when monitored by UV–visible spectroscopy. However, even on careful acidification, it was not found possible to prepare the corresponding acids which could be *fully* purified and characterised. However, the preparation of 2-carboxydiphenylacetylene as a viscous glass by Castro and Stephens[24] could be repeated. The preparation of this acid by Letsinger *et al.*[26] was not a general method and they found that the acid readily cyclised to the corresponding 3-phenylisocoumarin and 3-benzylidenephthalide by intramolecular addition.

General.—All the products had IR, ^1H and ^{13}C NMR, and mass spectra in accord with the stated structures. The catalytic reduction used would be expected to give *syn*-addition and result in a (*Z*)-stilbene. The (*Z*)-structure was confirmed by examination of the ^1H NMR spectra ($J_{1,2}$ 11–14 Hz, *cf.* ref. 27) and of the UV[25] spectra. The solvents and DDM were prepared as previously described.[28,29]

Measurements.—The pK_a values and the rate coefficients for esterification with DDM were determined as described previously.[28,30] A Perkin-Elmer Lambda 5 UV–visible spectrophotometer was used in all the kinetic studies. The rate coefficients for the alkaline hydrolysis of the esters were measured as previously described.[31] The substrate and hydroxide anion concentrations were *ca.* 2×10^{-4} and 5×10^{-3} 1×10^{-1} mol dm^{-3}, respectively. The reactions were followed at the λ value showing maximum difference between substrate and product, *i.e.* 320–340 nm for the diphenylacetylenes and 280–290 nm for the stilbenes. The reactions were first order in both substrate and hydroxide. As reactions were carried out in an excess of base, the resulting first-order behaviour could be observed without deviation for three 'half-lives.' The products of the hydrolysis of the (*Z*)-2-methoxycarbonylstilbenes (the anions of the corresponding acids) were obtained quantitatively from preparative-scale reactions, and their identities were confirmed by spectral comparison with the acids in basic solution. As discussed previously the products of the hydrolysis of the 2-methoxycarbonyldiphenylacetylenes could not be converted into the acids without cyclisation. However, with the exception of the 4′-nitro ester, the spectral changes were those minor changes expected for hydrolysis of the methyl ester to the anion of the carboxylic acid. The 4′-nitro ester did not give, on monitoring of the UV–visible spectra, a simple isosbestic point on alkaline hydrolysis and a strong absorption at 600 nm developed, giving the solution a purple colour. Nucleophilic addition to activated acetylenes is known to occur[32] and the product of this reaction appears to be the anion of either the 4-nitrobenzyl 2-methoxycarbonylphenyl ketone or the corresponding carboxylate anion. The latter ketones would be the products of hydration of the acetylene and would be expected to have a pK_a value of the order of 12, *cf.* the pK_a value of $PhCH_2COPh$: 17.7 in DMSO.[33]

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