806. *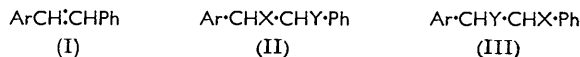Quantitative Aspects of Radical Addition. Part II.[1] The Orientation of the Addition of Trichloromethyl Radicals to Substituted* trans-*Stilbenes.*

By J. I. G. CADOGAN, (MRS.) ENID G. DUELL, and P. W. INWARD.

A quantitative study of the orientation of addition of trichloromethyl radicals to substituted *trans*-stilbenes has been carried out with the experimental procedure established in Part I,[1] whereby the isomeric mixture of 1 : 1 adducts of bromotrichloromethane and a substituted *trans*-stilbene is converted into the corresponding mixture of substituted α-phenylcinnamic acids. The composition of such mixtures has been determined by ultraviolet spectrophotometry. It is concluded that the orientation of addition is independent of selective polar effects and is governed by the high stability of the resulting intermediate benzyl-type radicals which is considered to vary little with the nature of nuclear substituents.

IN Part I of this series,[1] work was described leading to the establishment of the course of the reaction of bromotrichloromethane with *trans*-stilbene induced by di-t-butyl peroxide, and a method was established for determining accurately the extent of addition, by conversion of the 1 : 1 adduct of bromotrichloromethane and *trans*-stilbene into α-phenyl-*trans*-cinnamic acid. By these methods we have now studied the orientation of addition of trichloromethyl radicals (produced from bromotrichloromethane) to 3- and 4-substituted *trans*-stilbenes; reactions with 2-substituted analogues have not been studied since complications from steric hindrance were expected.

By analogy with the corresponding reaction with *trans*-stilbene, addition of bromotrichloromethane to a substituted stilbene (I) would be expected to give either or both of two adducts (II) and (III) (X = CCl_3, Y = Br) which on quantitative dehydrobromination

$$ArCH\dot{:}CHPh \qquad Ar\dot{\cdot}CHX\dot{\cdot}CHY\dot{\cdot}Ph \qquad Ar\dot{\cdot}CHY\dot{\cdot}CHX\dot{\cdot}Ph$$
$$(I) \qquad\qquad (II) \qquad\qquad\qquad (III)$$

and hydrolysis[1] would lead to the isomeric substituted α-phenylcinnamic acids. Determination of the isomeric composition of this mixture by ultraviolet spectrophotometry would then permit conclusions concerning the effect of nuclear substituents on the direction of addition of trichloromethyl radicals to the olefinic double bond. As a complement to such a study it was necessary to prepare the corresponding substituted phenylcinnamic acids in order to establish that they were stable under the standard conditions of work-up, and to provide standards for spectrophotometry. Addition of trichloromethyl radicals to the following *trans*-olefins has now been investigated: 3- and 4-nitro-, 3- and 4-bromo-, 3- and 4-methoxy-, 3- and 4-methyl-, 4-methoxy-4'-nitro-, and 3,4-dimethoxy-stilbene, and also 4-styrylpyridine. In some cases, discussed below, the significance of the results was reduced by side reactions.

EXPERIMENTAL

Ultraviolet spectrophotometric measurements were carried out with a Unicam S.P. 500 spectrophotometer.

Extracts were dried over anhydrous magnesium sulphate.

Bromotrichloromethane, di-t-butyl peroxide, and *trans*-stilbene were purified as described earlier.[1]

Preparation of Compounds.—Arylacetic acids. 4-Methylbenzyl alcohol,[2] m. p. 57—59°, was converted into the chloride, b. p. 86—87°/15 mm., by reaction with thionyl chloride and pyridine. *p*-Tolylacetic acid, m. p. 91—93° (lit.,[3] 93—94°), was obtained (89%) therefrom by

[1] Part I, Cadogan and Duell, preceding paper.
[2] Cadogan, Gold, and Satchell, *J.,* 1955, 561.
[3] Lewis and Elderfield, *J. Org. Chem.,* 1940, **5**, 290.

carboxylation of the Grignard reagent (Found: C, 71·5; H, 6·9. Calc. for $C_9H_{10}O_2$: C, 72·0; H, 6·7%). *p*-Methoxyphenylacetic acid, prepared by Elderfield and Meyer's method,[4] had m. p. 86—87° (Found: C, 65·2; H, 5·9. Calc. for $C_9H_{10}O_3$: C, 65·1; H, 6·0%). *m*-Bromophenylacetic acid, m. p. 94—96° (lit.,[5] 97°), *m*-tolylacetic acid, m. p. 58—60° (from ethanol) (lit.,[6] 61°) (Found: C, 71·8; H, 6·8. Calc. for $C_9H_{10}O_2$: C, 72·0; H, 6·7%), *m*-nitrophenylacetic acid, m. p. 116—118° (from ethanol) (lit.,[7] 116—117°), and *p*-bromophenylacetic acid, m. p. 112—113° (lit.,[8] 114—115°), were prepared by the Arndt–Eistert method. *p*-Nitrophenylacetic acid, m. p. 150—153° (lit.,[9] 151—152°), was prepared from benzyl chloride via *p*-nitrobenzyl chloride by Robertson's method.[9]

m-Methoxybenzaldehyde, b. p. 126—127°/25 mm., was prepared from the hydroxy-compound by using methyl toluene-*p*-sulphonate (cf. Buckles *et al.*[7]). *p*-Bromobenzaldehyde was prepared from diazotised *p*-bromoaniline by Beech's method.[10] *p*-Tolualdehyde was similarly prepared.

Preparation of Substituted α-Phenyl-trans-cinnamic Acids.—In general, these acids were prepared by a modification of the method described by Buckles *et al.*,[7] as follows: The aldehyde (1 mol.) and the acid (1 mol.) with triethylamine (1 mol.) or tri-n-propylamine (1 mol.) were heated with acetic anhydride (5 mol.). Mixtures including triethylamine were boiled under reflux for 48 hr. and those with tri-n-propylamine were heated on a steam-bath for 18 hr. After

TABLE 1.

Substituted α-phenyl-*trans*-cinnamic acids, $C_6H_4A\cdot CH\colon C(C_6H_4B)\cdot CO_2H$.

			Found (%)			Calc. (%)		Yield	$\lambda_{max.}$	$10^{-4} \times$
A	B	M. p.	C	H	Formula	C	H	(%)	(mμ)	$\epsilon_{max.}$
p-NO₂	H	215—215·5°	66·8	4·1	$C_{15}H_{11}NO_4$ [1, 9]	66·9	4·1	72		
H	*p*-NO₂	225—226	66·8	4·2	,, [2, 10]	,,	,,	34	270	1·853
p-Me	H	168	80·5	6·0	$C_{16}H_{14}O_2$	80·7	5·9	50	292	1·840
H	*p*-Me	151—151·5	80·9	5·6	,,	,,	,,	45	282	1·626
p-Br	H	209·5—210	59·6	3·7	$C_{15}H_{11}BrO_2$	59·4	3·6	79	286	1·818
H	*p*-Br	198	59·1	3·7	,,	,,	,,	79	284	1·565
p-MeO	H	193—194	75·7	5·4	$C_{16}H_{14}O_3$ [3]	75·6	5·5	61	298	1·954
H	*p*-MeO	160	75·5	5·4	,, [11]	,,	,,	64	272	1·368
m-NO₂	H	184—185	67·1	4·2	$C_{15}H_{11}NO_4$ [12]	66·9	4·1	60	262	1·969
H	*m*-NO₂	228·5—229	66·6	4·1	,,	,,	,,	61	272	2·046
m-Me	H	150—151	80·7	5·9	$C_{16}H_{14}O_2$	80·7	5·9	46	284	1·501
H	*m*-Me	134—135	80·6	5·9	,,	,,	,,	57	270	1·354
m-Br	H	169—170	59·1	3·7	$C_{15}H_{11}BrO_2$	59·4	3·6	62	292	2·169
H	*m*-Br	196—196·5	59·2	3·7	,,	,,	,,	43	278	1·517
m-MeO	H	195—196	75·8	5·5	$C_{16}H_{14}O_3$ [4]	75·6	5·5	63	284	1·398
H	*m*-MeO	156	75·4	5·4	,,	,,	,,	65	276	1·456
H	H	172·5	80·4	5·5	$C_{15}H_{12}O_2$ [5]	80·4	5·4			
H *	H	142	80·1	5·2	,, [6]	,,	,,			
p-NO₂	*p*-MeO	197—200	64·0	4·3	$C_{16}H_{13}NO_5$	64·2	4·35	55	226	1·634
p-MeO	*p*-NO₂	246	64·4	4·4	,, [7]	,,	,,	40	286	1·880
3,4-(MeO)₂	H	231—234	81·0	6·6	$C_{17}H_{16}O_4$ [8]	80·0	6·7	55		
H	3,4-(MeO)₂	156	80·2	6·8	,,	,,	,,	35		

* *cis*-Acid. [1-4] Ref. 7 gives m. p. (1) 212—214°, (2) 224—225°, (3) 189°, (4) 187—188°. [5] Ref. 11 gives m. p. 174°. [6] Ref. 11 gives m. p. 138°. [7] Hewitt, Lewcock, and Pope (*J.*, 1912, **101**, 604) give m. p. 231°. [8] Aulin-Erdtman and Erdtman (*Ber.*, 1941, **74**, 50) give m. p. 220°. [9] Found: N, 5·0. Calc.: N, 5·2%. [10] Found: N, 4·9%. [11] Found: N, 5·1. Reqd.: N, 5·2%. [12] Found: N, 5·3%.

dilution with water the mixture was boiled with benzene to give a clear solution, from which the acid was extracted with alkali. The basic extracts were boiled to expel benzene, cooled, and acidified (pH 3). The crude acid was purified by decolorisation with charcoal followed by recrystallisation, usually from ethanol, to constant m. p. The details of these experiments and the physical constants of the acids are given in Table 1.

[4] Elderfield and Meyer, *J. Amer. Chem. Soc.*, 1954, **76**, 1883.
[5] Mauthner, *J. prakt. Chem.*, 1917, **95**, 62.
[6] Radziszewski and Wispek, *Ber.*, 1885, **18**, 1282.
[7] Buckles, Bellis, and Coder, *J. Amer. Chem. Soc.*, 1951, **73**, 4972.
[8] Bedson, *J.*, 1880, **37**, 94.
[9] Robertson, *Org. Synth.*, Coll. Vol. I, 1st edn., pp. 396, 406.
[10] Beech, *J.*, 1954, 1297.

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α-Phenyl-*trans*- and -*cis*-cinnamic acid were prepared by Fieser's method.[11] α-p-*Methoxyphenyl*-p-*nitro*-trans-*cinnamic acid*, prepared similarly, was purified by crystallisation from ethanol to m. p. 197—200°.

p-Methoxy-α-*p*-nitrophenyl-*trans*-cinnamic acid was prepared as follows: *p*-Nitrophenylacetic acid (18 g., 0·1 mole) was converted into its sodium salt and boiled under reflux for 8 hr. with *p*-anisaldehyde (13·6 g., 0·1 mole) and acetic anhydride (50 g., 0·5 mole), cooled, and poured into aqueous ethanol. The resultant solid was washed with hot aqueous sodium carbonate, and the alkaline solution extracted with methylene chloride. This extract was washed with aqueous sodium carbonate and the alkaline solutions were acidified to give an orange acid (12 g., 40%), m. p. 239—242°. Recrystallisation from ethanol gave the cinnamic acid as yellow needles, m. p. 246°.

α-3,4-Dimethoxyphenyl-*trans*-cinnamic acid, m. p. 231—234° [from light petroleum (b. p. 60—80°)–chloroform], was similarly prepared from veratraldehyde; and α-3,4-*dimethoxyphenyl*-trans-*cinnamic acid*, m. p. 156° [from benzene–light petroleum (b. p. 40—60°)], similarly from sodium 3,4-dimethoxyphenylacetate.

Preparation of Monosubstituted trans-*Stilbenes.*—These were prepared by one of two general methods: (a) the Meerwein coupling reaction,[12] and (b) decarboxylation of the substituted α-phenyl-*trans*-cinnamic acid followed by isomerisation of the *cis*-stilbene so formed. In general, the second method was more satisfactory.

(a) *Modified general procedure for the Meerwein reaction.* A clear, filtered solution of the diazotised amine (1 mole) was added to a solution of cinnamic acid (1 mole) in acetone (1 l.) at 0—5°. Sodium acetate (2—3 moles) was added and, after its dissolution, a solution of cupric chloride (0·5 mole) in water (80 ml.). The stirred mixture was then allowed to attain room temperature, a gas being evolved. At the end of the reaction (3—4 hr.) the heterogeneous mixture was extracted with benzene (3 × 100 ml.), and the benzene solution was steam-distilled until the distillate was clear (*ca.* 1500 ml.). The residue in benzene (1 l.) was washed with 3N-ammonia to remove acids, and dried. Evaporation left the crude stilbene, which was purified by chromatography on alumina.

(b) *Decarboxylation.* Catalytic decarboxylation of the substituted α-phenyl-*trans*-cinnamic acid was carried out by the method of Buckles and Wheeler [13] with a copper chromite catalyst.

TABLE 2.

Preparation of substituted *trans*-stilbenes.

Stilbene & method	Yield (%)	M. p.*	Crystallised from	Found (%) C	H	Formula	Calc. (%) C	H
4-NO$_2$ (a)	49	155—156° ^{c}	EtOH	74·5	4·8	C$_{14}$H$_{11}$NO$_2$	74·7	4·9
4-NO$_2$ (b)	81	155—156 ^{c}	EtOH	—	—	—	—	—
4-Me (a)	28	118—119 ^{c}	EtOH	92·9	7·1	C$_{15}$H$_{14}$	92·8	7·2
4-Br (a)	15	139·5—140 ^{d}	Pet †	64·7	4·4	C$_{14}$H$_{11}$Br	64·9	4·2
4MeO (b)	78	135—135·5 ^{c}	EtOH	85·9	6·7	C$_{15}$H$_{14}$O	85·7	6·7
3-NO$_2$ (a)	28	112 ^{c}	EtOH	74·6	5·0	C$_{14}$H$_{11}$NO$_2$	74·7	4·9
3-Me (a)	14	47—48 ^{c}	MeOH	92·7	7·0	C$_{15}$H$_{14}$	92·8	7·2
3-Br (a)	14	89—90 ^{d}	EtOH	65·1	4·1	C$_{14}$H$_{11}$Br	64·9	4·2
3-Br (b)	74	89—90 ^{d}	EtOH	—	—	—	—	—
3-MeO ‡ (b)	83	32—33 ^{f}		85·6	6·6	C$_{15}$H$_{14}$O	85·7	6·7
4-MeO-4'-NO$_2$...	40	133—134 ^{g}	EtOH	70·5	5·1	C$_{15}$H$_{13}$NO$_3$	70·6	5·1
3,4-(MeO)$_2$	60	109 ^{h}	C$_6$H$_6$–Pet †	80·2	6·8	C$_{16}$H$_{16}$O$_2$	80·0	6·7

* In substantial agreement with recorded values.   † Light petroleum (b. p. 60—80°).   ‡ Purified by distillation, b. p. 130—132°/10^{-2} mm., and recrystallisation from light petroleum (b. p. 60—80°).
^{c} Ref. 12. ^{d} Bergmann, Weizman, and Shapiro (*J. Org. Chem.*, 1944, **9**, 408). ^{e} Bergmann and Shapiro (*ibid.*, 1947, **12**, 57). ^{f} New compound. ^{g} Calvin and Alter (*J. Chem. Phys.*, 1951, **19**, 765). ^{h} Ref. 14.

The crude *cis*-stilbene was boiled (15 mm.) with the minimum amount of nitrobenzene in the presence of a crystal of iodine. In some cases the *trans*-isomer separated on cooling; in all cases the nitrobenzene was removed by distillation and the residue purified by chromatography.

The results of these preparations are summarised in Table 2.

trans-3,4-Dimethoxystilbene (60%), prepared by the method of Aulin-Erdtman and

[11] Fieser, *J. Chem. Educ.*, 1954, **31**, 291.
[12] Meerwein, Buchner, and van Emster, *J. prakt. Chem.*, 1939, **152**, 237.
[13] Buckles and Wheeler, *Org. Synth.*, 1953, **33**, 88.
[14] Aulin-Erdtman and Erdtman, *Ber.*, 1941, **74**, 50.

Erdtman [14] from veratraldehyde, phenylacetic acid, lead monoxide, and acetic anhydride, had m. p. 109° after recrystallisation from benzene–light petroleum (b. p. 60—80°).

4-Styrylpyridine, m. p. 129·5—130° (Found: N, 7·9. Calc. for $C_{13}H_{11}N$: N, 7·75%), was prepared as described by Kaslow and Stayner,[15] who reported m. p. 127°.

Free-radical Addition of Bromotrichloromethane to Substituted trans-*Stilbenes.*—Reactions were carried out in duplicate under nitrogen at 105° for 72 hr. The molar ratio, stilbene : bromotrichloromethane : di-t-butyl peroxide was 1 : 11 : 0·5. The olefin–halide mixture was allowed to attain 105° before the addition of the peroxide, which was washed in with a small amount of halide. The weight of stilbene was generally 4 g. The general method of working up to give the isomeric mixture of substituted α-phenyl-*trans*-cinnamic acids and unchanged *trans*-stilbene has been described in Part I.[1] An innovation in this case involved removal of the excess of solvent, to give a residue which was made up to a standard volume (100 ml.) in acetone. This enabled several determinations to be made on each reaction mixture. The entire yield of acidic product was in turn made up to a standard volume in " AnalaR " ethanol, and this homogeneous mixture was analysed by ultraviolet spectrophotometry (see below). The results are summarised in Table 4 below. The conversions of *trans*-stilbene into acidic product were of the order of 50—80% and the accountance of the *trans*-stilbene in terms of acidic product and unchanged stilbene varied from 92% to 96% in all cases except those discussed below.

Anomalous results were obtained from the reaction with *trans*-4-methoxystilbene; the recovery was 84%, the reaction mixture with perchloric acid was purple, and a gum, b. p. 210—220°/10^{-2} mm., was obtained [Found: C, 85·6; H, 6·1; MeO, 16·1. $(C_{15}H_{14}O)_n$ requires C, 85·7; H, 6·7; MeO, 15·8%]. A series of complementary experiments, in which the effect of the perchloric acid–acetic acid treatment on the products of the above reaction was examined, indicated that the isomeric *p*-methoxy-α-phenyl-*trans*-cinnamic acids were partially decarboxylated in the presence of the mixture of acids, that *cis*-4-methoxystilbene became isomerised to the *trans*-form, and that gums, formulated as the dimer of 4-methoxystilbene, were formed.

Reaction of trans-4-*Methoxystilbene with Phosphoric Pentoxide.*—The stilbene (1·00 g.) with phosphorus pentoxide (10 g.) in xylene (100 ml.; Na-dried) was boiled under reflux for 8 hr. (cf. Battersby and Binks [16]) and poured on ice (200 g.). The organic layer was washed with 2N-hydrochloric acid and dried. The residue, after removal of the low-boiling material, gave *trans*-4-methoxystilbene (0·36 g.), b. p. 124—126°/10^{-2} mm., m. p. and mixed m. p. 129—132°, and a yellow syrup (0·63 g.), b. p. 208—210°/10^{-2} mm. (Found: C, 85·5; H, 6·5. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%). The infrared spectrum of this material was very similar to that of the " dimer " obtained from experiments described above.

A mixture of α-3,4-dimethoxyphenyl-*trans*-cinnamic acid and 3,4-dimethoxy-α-phenyl-*trans*-cinnamic acid on treatment with perchloric acid in acetic acid was extensively decomposed under the standard conditions of working up. *p*-Methoxy-α-*p*-nitrophenyl-*trans*-cinnamic acid gave 4-methoxy-4'-nitro-*trans*-stilbene (88%) on similar treatment. The substituted cinnamic acids corresponding to all other stilbenes studied were stable under the conditions of working up.

The radical-induced reaction of bromotrichloromethane with 4-styrylpyridine was anomalous, the only product being a high-melting intractable solid of ionic character.

Determination of the Ratios of Isomers.—The method was based on that of Cadogan, Hey, and Williams.[17] The spectra of standard solutions in ethanol of the mixtures of isomeric acids (*ca.* $2·5 \times 10^{-5}$ mole l.$^{-1}$) were recorded in the range 220—320 mμ, as were the spectra of standard solutions in ethanol of each of the pure components. Each determination was repeated with a freshly prepared solution, to give a mean value for the molecular extinction coefficient ε.

The composition of the mixture was calculated from the following pair of equations: $\varepsilon_{mixture} = x\varepsilon_1 + y\varepsilon_2$; ε' mixture $= x\varepsilon_1' + y\varepsilon_2'$; where x and y are the fractions of isomers 1 and 2 in the mixture, $\varepsilon_{mixture}$, ε_1, and ε_2 are the extinction coefficients of the mixture, pure isomer 1, and pure isomer 2 at a given wavelength, and ε' values are those at another wavelength. The nine pairs of wavelengths which were selected for each mixture all lay around the absorption maxima for the pure isomers. A mean value for the composition of each mixture was then obtained. The results, summarised in Table 4, show that values for the percentage

[15] Kaslow and Stayner, *J. Amer. Chem. Soc.*, 1945, **67**, 1716.
[16] Battersby and Binks, *J.*, 1958, 4333.
[17] Cadogan, Hey, and Williams, *J.*, 1954, 794.

composition of the mixtures total 99—100, confirming the view that the mixtures contain only the relevant pair of isomeric acids. Further, to confirm that the mean values (x, y) given in Table 3 represented the true value for the composition, they were used to predict values for $\varepsilon_{\text{mixture}}$ at a number of wavelengths other than those used to determine x and y, by substitution in one of the equations given above. The accuracy of the determination was also tested by the analysis of mixtures of known composition and deviations due to non-adherence either to

TABLE 3.

Analysis of mixtures of known composition.

| | Composition (%) | | | | | Composition (%) | | | |
| | CHPh:CAr·CO₂H | | CHAr:CPh·CO₂H | | | CHPh:CAr·CO₂H | | CHAr:CPh·CO₂H | |
Subst.	Found	Calc.	Found	Calc.	Subst.	Found	Calc.	Found	Calc.
4-NO₂	41·4	42·0	57·6	58·0	3-NO₂	44·6	45·2	55·1	54·8
4-Me	60·8	60·5	38·6	39·5	3-Me	50·9	51·4	49·1	48·6
4-Br	50·0	50·5	49·0	49·5	3-Br	50·9	50·6	49·1	49·4
4-MeO	50·0	50·5	49·7	49·5	3-MeO ...	50·8	51·3	49·0	48·7

Beer's law or to the principle of additivity of optical densities could be detected. The results of such accuracy determinations were satisfactory.

DISCUSSION

The results of the present investigation, expressed in terms of the isomeric composition of the mixture of substituted α-phenylcinnamic acids produced from the corresponding substituted stilbenes, are summarised in Table 4, where the position of the carboxyl group in the acid corresponds to the initial position of attack by the trichloromethyl radical on the stilbene.

TABLE 4.

Addition of trichloromethyl radicals to substituted *trans*-stilbenes.

| | Composition (%) | |
X in X·C₆H₄·CH:CHPh	X·C₆H₄·CH:CPh·CO₂H	X·C₆H₄·C(CO₂H):CHPh
4-NO₂	60	40
4-Br	53	47
4-MeO *	43	56
3-NO₂	53	47
3-Me	44	55
3-Br	55	45
3-MeO	52	48

* Side-reactions occurred in this case.

In general, the orientation of addition of a free radical (X·) to an unsymmetrically substituted olefin, RCH:CHR′, would be expected to be influenced by steric factors, polar effects, and/or the relative stability of the possible intermediate radicals ·CHR·CHXR′ and CHXR·CHR′·. In the system used in this investigation steric factors are considered to be unimportant, since they are likely to apply equally to both olefinic carbon atoms so that discussion of the experimental results can be confined to the possible influences of polar and radical-stability factors. Little is known about the importance of polar effects in free-radical additions, although there is evidence that the trichloromethyl radical can be considered to be electron-accepting.[18] The results given in Table 4 show, however, that a selective polar effect is not operative in the reactions with substituted stilbenes, since there is no significant variation in position of attack with change of polarity or position of the nuclear substituent. On the other hand, if it is assumed that the trichloromethyl radical is an electron-acceptor, it is possible that an overall deactivation of the double bond in the nitro-stilbenes, say, might be operating during the addition as a result of the electron-withdrawing nature of the nitro-group, while the converse might occur with the methoxy- and methyl-stilbenes. A polar effect of this nature could be detected only by measurement

[18] Cadogan and Hey, *Quart. Revs.*, 1954, **8**, 308; Walling, " Free Radicals in Solution," J. Wiley & Sons, New York, 1957.

of rates of reaction of substituted stilbenes relative to a standard such as stilbene itself. Whatever the outcome of such experiments, which will be reported in a later paper, it is clear, however, that the orientation, if not the rate, of attack of trichloromethyl radicals on substituted stilbenes is independent of the polar nature of the nuclear substituent.

The absence of marked substituent effects in this reaction indicates, however, that addition to stilbene is governed largely by the stability of the resulting intermediate free radical. Thus, for 3-substituted stilbenes there is no difference in stability between the two possible radicals in each case, since delocalisation of the benzylic free electrons with the non-conjugated 3-substituent cannot occur. In the case of 4-substituted stilbenes, particularly if the substituent is able to enter into conjugation such as nitro- or methoxyl, greater stability of radical (IV) than of (V) might be expected as a result of the possible additional delocalisation of the free electron in this case.

In agreement with this, the largest real effect was observed with 4-nitro-*trans*-stilbene and the orientation was as predicted. It is clear, however, that delocalisation which arises from 4-substituents is low, *i.e.*, the differences in stability between substituted benzyl radicals are small.

The orientation of addition to 4-methoxy-*trans*-stilbene, in the light of the foregoing discussion, appears to be anomalous, but the result is considered to have little significance as a result of side-reactions which occurred under the influence of perchloric acid during the working up (see p. 4167). Battersby and Binks [16] obtained the dimer of 3,4,3′,4′-tetramethoxystilbene, formulated as either a tetraphenylcyclobutane derivative or an indane, from the monomer by the action of phosphorus pentoxide in boiling toluene. Application of their method to 4-methoxy-*trans*-system gave a corresponding dimeric product of the same physical characteristics as that isolated from the corresponding reaction with
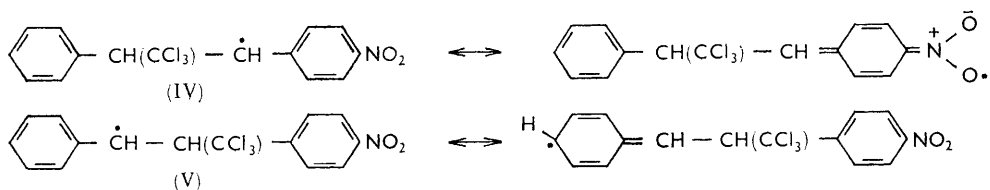
perchloric acid in acetic acid. It is therefore probable that the product of this reaction was one or a mixture of the possible dimethoxytetraphenylbutanes which can exist in many stereoisomeric forms or the corresponding indane. The acids derived from 3,4-dimethoxy-*trans*-stilbene and 4-nitro-4′-methoxy-*trans*-stilbene were also readily decarboxylated by perchloric acid in acetic acid, although products of high molecular weight were obtained only in the former case. The acids derived from 3-methoxystilbene, on the other hand, were stable and no dimer formation from 3-methoxy-*trans*-stilbene was detected.

Directive effects in stilbenes containing the 4-methoxy-group could not, therefore, be determined by our method, nor could those operative in addition to 4-methyl-*trans*-stilbene, which gave irreproducible results. In the latter case it is believed that interaction with the aliphatic side chain occurred, but discussion is deferred. Orientation effects in addition of trichloromethyl radicals to 4-styrylpyridine were also impossible to obtain by our method, since interaction of the pyridine residue with bromotrichloromethane appeared to be the preferred reaction, the nature of which is under investigation.

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