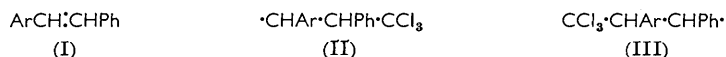**807.** *Quantitative Aspects of Radical Addition. Part III.*[1] *Relative Rate Ratios for the Addition of Trichloromethyl Radicals to Substituted Stilbenes, Phenanthrene, and* trans-β-*Methylstyrene.*

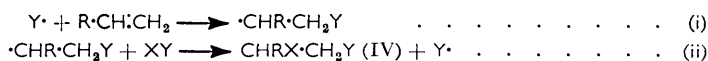By J. I. G. CADOGAN and P. W. INWARD.

Addition of alkyl radicals to the 9,10-double bond of phenanthrene has been demonstrated for the first time by conversion of the adduct obtained from the radical-induced reaction of the hydrocarbon with bromotrichloromethane into phenanthrene-9-carboxylic acid. Relative rate ratios for addition of trichloromethyl radicals to substituted stilbenes, phenanthrene, and *trans*-β-methylstyrene have been measured by means of competition experiments in which pairs of olefins compete for a limited quantity of trichloromethyl radicals generated by decomposition of di-t-butyl peroxide in bromotrichloromethane. These rate ratios lead to the conclusion that the relative rates of addition are independent of polar factors and are governed by the stability of the intermediate free radicals.

IN Part II of this series,[1] directive effects were studied for the addition of trichloromethyl radicals to substituted *trans*-stilbenes (I) and it was concluded that the direction of addition was largely, and probably entirely, independent of the polar nature of nuclear substituent groups in the stilbene; also that the small effects observed were a function of the relative stabilities of the intermediate free radicals (II) and (III).

$$\text{ArCH:CHPh} \qquad \text{·CHAr·CHPh·CCl}_3 \qquad \text{CCl}_3\text{·CHAr·CHPh·}$$
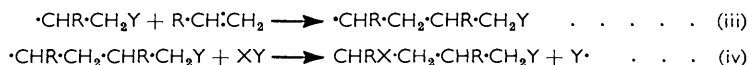$$\text{(I)} \qquad\qquad\qquad \text{(II)} \qquad\qquad\qquad \text{(III)}$$

However, to obtain a complete description of radical addition to an olefinic double bond, a knowledge of the overall rate of attack at the double bond relative to a standard, *e.g.*, *trans*-stilbene, is required in addition to information concerning the position of attack. For example, it is conceivable in the case of *trans*-4-nitrostilbene that, although no *selective* polar effects are operative in its reaction with trichloromethyl radicals, the double bond might be deactivated relative to that in *trans*-stilbene. This could arise from a non-selective lowering of the electron density at the double bond, so that attack by the electron-accepting trichloromethyl radical would be less favoured than attack on stilbene. In such circumstances the direction of attack would be determined by resonance stability factors, while polar factors would influence its rate. Relative rates of attack of trichloromethyl radicals on some relevant compounds have therefore been determined, with results described in this paper.

Free-radical chain addition of a molecule XY to an olefin involves an addition (i), followed by a displacement (ii):

$$\text{Y· + R·CH:CH}_2 \longrightarrow \text{·CHR·CH}_2\text{Y} \qquad \dots\dots\dots \text{(i)}$$
$$\text{·CHR·CH}_2\text{Y + XY} \longrightarrow \text{CHRX·CH}_2\text{Y (IV) + Y·} \qquad \dots\dots\dots \text{(ii)}$$

For a comparison of reactivities of olefins with respect to radical addition [reaction (i)] this step must be rate-determining; thus reagents (XY) which react rapidly in step (ii) must be selected. This type of reagent has incidentally the advantage of minimising telomer formation [(iii) and (iv)]:

$$\text{·CHR·CH}_2\text{Y + R·CH:CH}_2 \longrightarrow \text{·CHR·CH}_2\text{·CHR·CH}_2\text{Y} \qquad \dots\dots \text{(iii)}$$
$$\text{·CHR·CH}_2\text{·CHR·CH}_2\text{Y + XY} \longrightarrow \text{CHRX·CH}_2\text{·CHR·CH}_2\text{Y + Y·} \qquad \dots \text{(iv)}$$

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[1] Part II, Cadogan, Duell, and Inward, *J.*, preceding paper.

There is ample evidence that bromotrichloromethane is such a reagent [2] provided it is present in excess, and this was used by Kharasch and his co-workers [3] in the first measurements of relative rates of attack of trichloromethyl radicals on a series of olefins. The competition method was used and the mixture of adducts (IV; X = Br, Y = CCl$_3$) was isolated by distillation and analysed by halogen or refractive-index determinations. These methods are, however, very sensitive to the presence of the products of side reactions, such as dehydrobrominated compounds, which could be formed by decomposition on distillation, and were not considered satisfactory for our purpose.

In previous Parts a method of quantitative conversion of the 1 : 1 adducts, formed by radical-chain addition of bromotrichloromethane to substituted stilbenes, into the corresponding α-phenylcinnamic acids was described, and the theoretical and the practical advantages of the system, in which an excellent balance of olefin was obtained in most cases, were discussed. In the present investigation pairs of such stilbenes and of related compounds were allowed to react, in competition, with a limited amount of trichloromethyl radicals generated by decomposition of di-t-butyl peroxide in an excess of bromotrichloromethane. The resulting mixture of adducts was converted into the corresponding mixture of acids, which was then analysed by titration. The relative rate ratio K_S^B for the competition of two olefins B and S with trichloromethyl radicals was then calculated on the following basis:

$$S + \cdot CCl_3 \xrightarrow{k_S} \text{Product}$$

$$B + \cdot CCl_3 \xrightarrow{k_B} \text{Product}$$
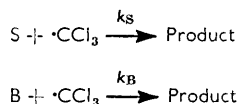
Then

$$-d[S]/dt = k_S[\cdot CCl_3][S]$$

Hence

$$K_S^B = k_B/k_S = (\log [B_0] - \log [B])/(\log [S_0] - \log [S])$$

where [B$_0$] and [B] are the initial and the final concentration of olefin B, and similarly for S.

The substituted stilbenes which have been studied in this investigation contained 3- or 4-substituents only, so that steric influences on the rate of reaction of trichloromethyl radicals with the double bond could be ignored.

Experimental

Extracts and solutions were dried over magnesium sulphate.

Preparation of Compounds.—Bromotrichloromethane, di-t-butyl peroxide, *trans*-stilbene, and *NN*-dimethylformamide were purified as described by Cadogan and Duell.[4] *cis*-Stilbene, *trans*-4-nitrostilbene, *trans*-3-nitrostilbene, α-phenyl-*trans*- and -*cis*-cinnamic acid, *p*-bromobenzaldehyde, and *p*-bromophenylacetic acid were prepared and purified as previously described.[1,4] Nitromethane was dried, boiled under reflux first in a stream of nitrogen (2 hr.), then over activated charcoal (1 hr.), and distilled through a 3-ft. helix-packed column fitted with a variable take-off head. The fraction of b. p. 101° was collected, stored over magnesium sulphate, and redistilled before use. Methylene chloride was washed four times with 5% sodium carbonate solution and with water, dried, distilled, and stored in a dark bottle.

trans-β-2-Naphthylstyrene, m. p. 150° [from light petroleum (b. p. 60—80°)], was prepared by the method of Everett and Kon [5] who reported m. p. 150° (Found: C, 94·3; H, 5·7. Calc.

[2] Cadogan and Hey, *Quart. Rev.*, 1954, **8**, 308; Cadogan, Roy. Inst. Chem. Lecture Series, 1961, No. 6; Melville, Robb, and Tutton, *Discuss. Faraday Soc.*, 1953, **14**, 150.

[3] Kharasch and Friedlander, *J. Org. Chem.*, 1949, **14**, 239; Kharasch and Sage, *ibid.*, p. 537; Kharasch, Simon, and Nudenberg, *ibid.*, 1953, **18**, 328.

[4] Cadogan and Duell, *J.*, 1962, 4154.

[5] Everett and Kon, *J.*, 1948, 1601.

for $C_{18}H_{14}$: C, 93·9; H, 6·1%). 4-Nitro-*cis*-stilbene (m. p. 59—63°) was kindly prepared by Mr. D. M. Cooke by Campbell and McDonald's method; [6] it was separated from the *trans*-isomer by fractional crystallisation from ethanol and chromatography on alumina as described below, and recrystallised from light petroleum (b. p. 40—60°); Weygand and Gabler [7] reported m. p. 65°.

trans-4-Methylstilbene was prepared as follows: *p*-Tolualdehyde (24·2 g.) was added in ether (25 ml.) to benzylmagnesium chloride (from 25·3 g. of halide) in ether (70 ml.) at 0°. The mixture was poured into ice and acetic acid. The resulting solid was extracted into ether which was washed with brine, saturated aqueous sodium hydrogen carbonate, aqueous sodium hydrogen sulphite, and again brine, and dried. The residue, after removal of the solvent, was boiled under reflux in acetic anhydride (30 ml.) for 3 hr., the solvent was removed at 15 mm., and the residue recrystallised from methanol, to give *trans*-4-methylstilbene in plates, m. p. 118—120° (lit.,[8] 117°). Evaporation of the mother-liquor gave a residue which was boiled under reflux with light petroleum (b. p. 100—120°) and a crystal of iodine for 2 hr. Removal of the solvent followed by recrystallisation of the residue from methanol gave more *trans*-4-methylstilbene, m. p. 117—119° (total 12 g.).

Three methods of preparation of *trans*-4,4′-dibromostilbene were investigated. (i) The method of Stanfield and Reynolds,[9] involving copper powder and *p*-bromo(thiobenzaldehyde), gave *trans*-4,4′-dibromostilbene (29%) m. p. 212° (from benzene–ethanol). (ii) 4-Bromobenzyl bromide, prepared by the general method of Schmid and Karrer [10] from *p*-bromotoluene and *N*-bromosuccinimide, was converted into 4-bromobenzyltriphenylphosphonium bromide, m. p. 260°, which, with *p*-bromobenzaldehyde (1 mol.) and ethanolic sodium ethoxide (1·1 mol.), followed by water, gave a precipitate which was recrystallised from ethanol. The yield of *trans*-4,4′-dibromostilbene varied from 3% to 40%. (iii) A modification of the method of Bance, Barber, and Woolman [11] was most satisfactory. Bibenzyl (78 g.; m. p. 50—53° after recrystallisation from methanol) was boiled in acetic acid (930 ml.) and water (35 ml.) with bromine (284·5 g.) under reflux until no more solid separated (1·25 hr.). The hot mixture was filtered and the residual α,α′,4,4′-tetrabromobibenzyl was washed with acetic acid, ethanol, and ether; it had m. p. 235—245° (decomp.) (72·4 g.). This bromide (37·5 g.) was boiled with cuprous bromide (27·5 g.) under reflux in pyridine (75 ml.) for 1 hr., then poured into hydrochloric acid (*d* 1·18; 400 ml.). The next day the solid was collected and washed with hydrochloric acid and with water. Recrystallisation from acetic acid and then benzene–light petroleum (b. p. 60—80°) gave *trans*-4,4′-dibromostilbene (9 g.), m. p. 215—216° (Found: C, 50·2; H, 3·35; Br, 46·7. Calc. for $C_{14}H_{10}Br_2$: C, 49·7; H, 3·0; Br, 47·2%). Stanfield and Reynolds [9] reported m. p. 206°.

3,5-Dimethylbenzyl bromide (76%), prepared by Schmid and Karrer's method [10] from mesitylene and *N*-bromosuccinimide, had b. p. 112—120°/15 mm., m. p. 29°. Wispek [12] reported m. p. 34—35°. The bromide (30 g.), with hexamethylenetetramine (21·8 g.) in aqueous ethanol (60% v/v; 70 ml.) containing 40% formaldehyde solution (14 ml.), was boiled under reflux for 18 hr., then steam-distilled. The distillate was diluted with water (2 vols.) and extracted with methylene chloride. The extract was washed with 2N-sulphuric acid (2 × 100 ml.), 2N-sodium hydroxide (100 ml.), and water (2 × 200 ml.) and dried. Distillation gave 3,5-dimethylbenzaldehyde, b. p. 109—111°/15 mm. (14·5 g., 75%).

3,5-Dimethylbenzyl bromide (18 g.) was converted into the nitrile, which was boiled with potassium hydroxide (24 g.) in water (30 ml.) and ethanol (150 ml.) until evolution of ammonia ceased (16 hr.). Ethanol was removed by distillation, water (200 ml.) was added, and the aqueous layer washed with methylene chloride. Acidification of the aqueous layer gave crude 3,5-dimethylphenylacetic acid (8 g.), m. p. 90—100° (lit.,[13] 99·5—100·5°).

α-(3,5-*Dimethylphenyl*)-*trans*-*cinnamic acid*, prepared (40%) by the general method of Buckles and Hausman [14] from 3,5-dimethylphenylacetic acid (8 g.), benzaldehyde (5·3 g.),

[6] Campbell and McDonald, *J. Org. Chem.*, 1959, **24**, 1246.
[7] Weygand and Gabler, *Ber.*, 1938, **71**, 2474.
[8] Späth, *Monatsh.*, 1914, **35**, 469.
[9] Stanfield and Reynolds, *J. Amer. Chem. Soc.*, 1952, **74**, 2878.
[10] Schmid and Karrer, *Helv. Chim. Acta*, 1946, **29**, 573.
[11] Bance, Barber, and Woolman, *J.*, 1943, 1.
[12] Wispek, *Ber.*, 1883, **16**, 1577.
[13] Gilman, Pacevitz, and Baine, *J. Amer. Chem. Soc.*, 1940, **62**, 1514.
[14] Buckles and Hausman, *J. Amer. Chem. Soc.*, 1948, **70**, 415.

triethylamine (5·0 g.), and acetic anhydride (15·3 g.), had m. p. 164° (from aqueous ethanol) (Found: C, 80·6; H, 6·9. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%).

3,5-*Dimethyl-α-phenyl*-trans-*cinnamic acid*, prepared (50%) similarly from phenylacetic acid and 3,5-dimethylbenzaldehyde, had m. p. 180° [from benzene–light petroleum (b. p. 60—80°)] (Found: C, 81·2; H, 6·4%).

4-*Bromo-α*-p-*bromophenyl*-trans-*cinnamic acid*, prepared (27%) similarly from *p*-bromo-benzaldehyde and *p*-bromophenylacetic acid, had m. p. 195° [from chloroform–light petroleum (b. p. 60—80°)] (Found: C, 47·5; H, 2·5; Br, 41·8. $C_{15}H_{10}Br_2O_2$ requires C, 47·1; H, 2·6; Br, 41·8%).

Phenanthrene was recrystallised to constant m. p. 100—101°.

Commercial *trans*-β-methylstyrene was distilled and the fraction of b. p. 76°/18 mm. was shown by gas–liquid chromatography to be of 99% purity. A sample of phenanthrene-9-carboxylic acid, m. p. 264°, was kindly provided by Professor D. H. Hey, F.R.S.

General Procedure for Competitive Addition Reactions of Bromotrichloromethane with Stilbenes and Related Compounds.—An equimolar mixture of two stilbenes, dissolved in a large excess of bromotrichloromethane, was allowed to compete for a small amount of trichloromethyl radicals. The amount of di-t-butyl peroxide was calculated to give between 10 and 50% conversion of the stilbenes into 1 : 1 adducts. Working-up was based on that described by Cadogan and Duell [4] who established that stilbenes could be accounted for in terms of substituted α-phenylcinnamic acids and unchanged stilbene for additions to a number of stilbenes. The mixture of substituted α-phenylcinnamic acids obtained was titrated in aqueous ethanol (50% w/w) against *ca.* 0·04N-sodium hydroxide, previously standardised against " AnalaR " potassium hydrogen phthalate. The usual precautions against entry of carbon dioxide were taken, an automatic burette (Griffin and George model 543-145) was used, and the sodium hydroxide solutions were transferred from the reservoir to the burette by nitrogen pressure. The titration was followed by noting the change of pH. A four-necked titration vessel was used. Into three of the necks were fitted the glass electrode, calomel electrode, and resistance thermometer. The burette was supported so that its tip was thrust a little way into the fourth neck, which also provided the inlet for a jet of nitrogen playing over the surface of the liquid. The titration mixture was stirred magnetically. Thus could be obtained a measure of the number of g.-equiv. of acid, and hence the composition of the mixture. The accuracy of the method was tested and shown to be satisfactory by titration of mixtures of substituted α-phenylcinnamic acids of known composition.

Choice of a Standard.—Initially *trans*-3-nitrostilbene was used as a standard in the competition experiments, *e.g.*, this stilbene was allowed to compete with *trans*-stilbene for trichloromethyl radicals and the resulting mixture of 1 : 1 adducts of these stilbenes with bromotrichloromethane was converted by the standard procedure (see below) into a mixture of α-phenyl-*trans*-cinnamic, α-*m*-nitrophenyl-*trans*-cinnamic, and 3-nitro-α-phenyl-*trans*-cinnamic acids. However, the molecular weights of the components, *i.e.*, unsubstituted and nitro-substituted phenylcinnamic acids, and hence the titres corresponding to the pure acids, were insufficiently far apart to allow accurate estimation of a mixture of the components. *trans*-4,4′-Dibromo-stilbene and β-methylstyrene, being of differing molecular weight, were therefore employed as standards in the competitive experiments. The standard method of working-up was successful in the latter case but was modified for experiments with *trans*-4,4′-dibromostilbene as a result of the insolubility of this compound and the resulting dibromophenylcinnamic acid. The revised method is exemplified below.

Competition Reaction of trans-*Stilbene and* trans-4,4′-*Dibromostilbene with Bromotrichloromethane.*—*trans*-Stilbene (3·604 g., 0·02 mole), 4,4′-dibromo-*trans*-stilbene (6·760 g., 0·01 mole), bromotrichloromethane (119·8 g., 0·605 mole), and di-t-butyl peroxide (0·047 g., 3·19 × 10⁻⁴ mole) were kept at 105° under nitrogen for 3 days. The excess of solvent was removed by distillation under nitrogen (20 mm.), and the solid residue, dissolved in benzene, was made up to one l. in benzene. Two aliquot parts (200 ml.) were taken and the solvent was removed by distillation. Each residue was then treated as follows: the residue was heated in *NN*-di-methylformamide (30 ml.) with pre-dried lithium chloride (1·1 g.) under calcium chloride guard-tubes on a steam-bath for 4 hr. The mixture was poured into water (400 ml.) and extracted with chloroform (200 + 6 × 30 ml.), and the extracts were dried. The drying agent was removed by filtration through a sintered-glass funnel, washed with chloroform, dissolved in water, and re-extracted with chloroform (3 × 20 ml.). This extract was dried,

and the drying agent was collected and washed with chloroform. The chloroform filtrates and washings were combined, solvent was removed by distillation, and the residue was boiled under reflux for 14 hr. with acetic acid (40 ml.) and 60% perchloric acid (2 ml.), then poured into water (600 ml.). The mixture was extracted with benzene (100 + 7 × 20 ml.), and the benzene solution was washed with water (25 ml.) and extracted with hot (50°) saturated aqueous sodium hydrogen carbonate until acidification of an extract produced no cloudiness. The combined alkaline solutions were washed with methylene chloride (2 × 20 ml.) and acidified with hydrochloric acid (*d* 1·18). The acid was extracted with methylene chloride (50 + 6 × 25 ml.) and the extracts dried. The drying agent was collected, washed with methylene chloride, dissolved in water, and re-extracted with methylene chloride (3 × 15 ml.). This extract was dried, freed from drying agent, and washed with methylene chloride. The combined filtrates and washings were evaporated to dryness and the residue was dried to constant weight over potassium hydroxide *in vacuo* [two experiments: (i) 0·4808 g.; (ii) 0·4510 g., corresponding to *ca.* 20% conversion]. The acidic mixture was analysed by titration as described above. The results of this experiment and of related competition experiments are given in Table 1.

TABLE 1.

Competition reactions of olefins with trichloromethyl radicals.

Subst. in olefins (mole)		CBrCl₃ (mole)	(BuᵗO)₂ (10⁻⁴ mole)	Reaction (%, approx.)	Acid mixture (g.)	Acid in mixture derived from A (wt. %)	K_B^A
A: *trans*-stilbene	B: stilbene						
4,4'-Dibromo- (0·02)	*trans*-Unsubst. (0·02)	0·605	3·19	20	0·4808	60·7	0·88
					0·4510	62·4	0·97
4,4'-Dibromo- (0·01)	,, (0·01)	0·3075	3·345	40	0·4931	64·2	0·97
4,4'-Dibromo- (0·01)	,, (0·01)	0·309 *	6·78	30	0·3687	67·6	1·05
					0·3577	65·8	1·13
4,4'-Dibromo- (0·01)	*cis*-Unsubst. (0·01)	0·3055	2·34	50	0·6526	69·7	1·60
					0·6593	71·5	1·83
4,4'-Dibromo- (0·01)	*trans*-4-Nitro- (0·01)	0·3075	3·61	27	0·3344	59·8	1·06
					0·3477	61·0	1·12
4,4'-Dibromo- (0·01)	*cis*-4-Nitro- (0·01)	0·3075	4·26	30	0·3736	61·05	1·13
4,4'-Dibromo- (0·01)	*trans*-4-Methyl- (0·01)	0·3071	2·60	33	0·3938 †	72·0	1·81
4,4-Dibromo- (0·0086)	Phenanthrene (0·0192)	0·4085	2·10	5	0·0562	78·05	5·20
trans-PhCH:CHMe (0·02)	*trans*-4-Nitro- (0·02)	0·605	2·86	40	0·6313	52·6	2·32
trans-2-C₁₀H₇·CH:CHPh (0·01)	*trans*-PhCH:CHMe (0·01)	0·302	2·175	50	0·5125	69·9	1·59
					0·5435	68·8	1·58

* In the presence of nitromethane (0·603 mole). † The acidic fraction was semisolid and contained extraneous products.

Competition between trans-3,5-*Dimethylstilbene and* trans-β-*Methylstyrene.*—*trans*-3,5-Dimethylstilbene (2·0818 g., 0·01 mole), *trans*-β-methylstyrene (1·1828 g., 0·01 mole), bromotrichloromethane (61 g., 0·3075 mole), and di-t-butyl peroxide (0·038 g., 2·605 × 10⁻⁴ mole) were allowed to react in the usual way. Working-up by the standard procedure gave acids whose analysis indicated that more 3,5-dimethylstilbene had been consumed than had been originally present in the reaction mixture, suggesting the formation of extraneous products in this case.

Reaction of Phenanthrene with Bromotrichloromethane Induced by Di-t-butyl Peroxide.—Phenanthrene (1·00 g., 0·0056 mole), bromotrichloromethane (61 g., 0·3075 mole), and di-t-butyl peroxide (0·039 g., 2·59 × 10⁻⁴ mole) were kept at 105° under nitrogen for 3 days. The excess of solvent was removed at 20 mm. under nitrogen and the residue made up to 50 ml. in benzene. A portion (20 ml.) was evaporated to dryness and the residue (0·4752 g.) was chromatographed in 1 : 1 benzene–light petroleum (b. p. 60—80°) on alumina. Only impure phenanthrene was obtained. A second portion (20 ml.) of the standard solution was subjected to the standard method of working-up. The acidic product (0·0450 g.; m. p. 235—245°), after recrystallisation from benzene–light petroleum (b. p. 60—80°), had m. p. 257—261° undepressed on admixture with phenanthrene-9-carboxylic acid (m. p. 264°). The neutral product (0·3359 g.), on chromatography in 1 : 1 benzene–light petroleum (b. p. 60—80°) on alumina, gave phenanthrene (0·327 g.), m. p. and mixed m. p. 95—98°. 91% of the phenanthrene was accounted for.

Reaction of Bromotrichloromethane and cis-*4-Nitrostilbene Induced by Di-t-butyl Peroxide.*—
The addition was performed by the standard method, for *cis*-4-nitrostilbene (1·1254 g., 0·005
mole), bromotrichloromethane (30 g., 0·1512 mole), and di-t-butyl peroxide (0·0127 g., 8·69 ×
10^{-5} mole). After removal of solvent, the residue was made up to 100 ml. in benzene. An
aliquot part (50 ml.) was evaporated and the residue (0·597 g.) was chromatographed in benzene–
light petroleum (b. p. 60—80°) (15% v/v) and on alumina which was shielded from light.
cis-4-Nitrostilbene could not be detected but *trans*-4-nitrostilbene (0·51 g., 90·7%), m. p. and
mixed m. p. 158—159°, was isolated.

Attempted Thermal Isomerisation of cis-*4-Nitrostilbene.*—*cis*-4-Nitrostilbene (0·6194 g.) in
light petroleum (b. p. 100—120°; 50 ml.) was kept at 105° for 3 days. The excess of solvent
was removed by distillation and the residue was analysed by chromatography on alumina in
the dark. Elution with benzene–light petroleum (b. p. 60—80°) (15 v/v; 900 ml.) gave *cis*-4-
nitrostilbene (0·578 g., 93%), m. p. and mixed m. p. 62—64°. Elution with a further 400 ml.
of this solvent gave *trans*-4-nitrostilbene (0·05 g.), m. p. and mixed m. p. 157—159°.

Reaction of Carbon Tetrachloride and cis-*4-Nitrostilbene Induced by Dibenzoyl Peroxide.*—
cis-4-Nitrostilbene (1·121 g.), carbon tetrachloride (23·13 g.) and dibenzoyl peroxide (0·0416 g.)
were boiled under reflux for 3 days under nitrogen. Working-up as in the preceding case
gave *cis*- (0·96 g., 86%), and *trans*-4-nitrostilbene (0·1 g., 9%).

Stability of Substituted α-Phenyl-trans-*cinnamic Acids in the Carboxylation Reaction.*—The
pure substituted α-phenyl-*trans*-cinnamic and related acids which are the end-products of the
competitive reactions were subjected to the carboxylation reaction (perchloric–acetic acid)
and found to be stable.

DISCUSSION

The results of the present investigation, which in conjunction with those described in
previous Parts [1,4] represent the first quantitative analysis of relative reactivities of
particular positions in unsymmetrical non-terminal olefins with respect to free-radical
addition, are summarised in Table 2.

TABLE 2.

Relative reactivities (*trans*-stilbene = 1) of substituted stilbenes and related compounds
towards trichloromethyl radicals.

Olefin	Relative reactivity	Olefin	Relative reactivity
trans-Stilbene	1·0	*cis*-4-Nitrostilbene	0·83
cis-Stilbene	0·55	*trans*-4-Methylstilbene †	0·52
trans-4,4'-Dibromostilbene	0·94	*trans*-β-Methylstyrene	2·0
trans-4,4'-Dibromostilbene *	1·09	*trans*-β-2-Naphthylstyrene	3·2
trans-4-Nitrostilbene	0·86	Phenanthrene	0·18

* Addition performed in the presence of nitromethane (2·5 mol.) and bromotrichloromethane
(1 mol.). † Side-reactions occurred in this case.

The Table shows that *trans*-stilbene reacts twice as quickly as *cis*-stilbene with trichloro-
methyl radicals, whereas *cis*- and *trans*-4-nitrostilbene are of comparable reactivity. This
is partially explained by the observation that isomerisation of *cis*-4-nitrostilbene to the
thermodynamically more stable *trans*-isomer occurred during the reaction. Presumably
this occurred also with *cis*-stilbene although to a smaller extent. The isomerisation was,
however, more easily observed in the reactions involving the nitrostilbenes because of the
ease of separation of the isomers on alumina. For this reason experiments designed to
show the cause of the isomerisation were carried out with *cis*-4-nitrostilbene. The recovery
(93%) of the *cis*-isomer from a solution in light petroleum after 3 days at 105° in the
absence of peroxide showed that the isomerisation could not be induced thermally to any
great extent. Nor could appreciable isomerisation be induced by decomposition of
dibenzoyl peroxide in a solution of *cis*-4-nitrostilbene in carbon tetrachloride. Since the
presence of trichloromethyl radicals in such a system has been demonstrated by the addition

of carbon tetrachloride to cyclohexene under these conditions,[15] it follows that the isomerisation of *cis*-4-nitrostilbene in bromotrichloromethane cannot occur by reversible addition of trichloromethyl radicals. Other species present during this reaction include t-butoxy-radicals and bromine atoms, the latter generated by spontaneous homolysis of bromotrichloromethane but there is no reason to suppose that t-butoxy-radicals are more likely to cause isomerisation than benzoyloxy-radicals, which do not.[16] The presence of bromine atoms in the standard system for the addition of bromotrichloromethane to stilbene has been shown by the isolation of 1,2-dibromo-1,2-diphenylethane,[4] and they have also been shown to cause the isomerisation of dimethyl maleate to fumarate.[17] Isomerisation of 1,2-dibromoethylene by bromine atoms has also been observed,[18] and it is known [19] that light and peroxides enormously accelerate the isomerisation of *cis*-stilbene in the presence of hydrogen bromide, evidently by a mechanism involving bromine atoms. The isomerisation which occurs during the reaction of bromotrichloromethane with *cis*-4-nitrostilbene is therefore attributed to reversible addition of bromine atoms. This conclusion appears, however, to conflict with the findings of Skell and Woodworth [20] who, in their studies on the photo-induced addition of bromotrichloromethane to *cis*- and *trans*-but-2-ene at 0—10°, did not observe isomerisation, despite the fact that photolysis of bromotrichloromethane generates trichloromethyl radicals and bromine atoms in equivalent amounts. It is clear, therefore, that generalisations concerning reversibility in reactions of this type cannot be made, particularly since the reactivity of *cis*-stilbene relative to the *trans*-isomer is significantly different from unity, the value to be expected if complete isomerisation had occurred before addition. Since isomerisation may occur in this reaction to a small but unknown extent, the relative rate ratio obtained for *cis*-stilbene must be considered to be a maximum figure.

The value obtained is, however, in good agreement with that of the relative reactivity of *cis*- compared with *trans*-stilbene in other free radical reactions. Szwarc and his colleagues [21] obtained a value of 0·28 for the addition of methyl radicals, and Lewis and Mayo [22] reported an approximate value of 0·5—0·67 obtained from rates of co-polymerisation of the two isomers with maleic anhydride. The reactivity of the *cis*-isomer relative to *trans*-stilbene with respect to benzoyloxy-radicals has also been found to be 0·5.[16] The higher reactivity of the *trans*-isomer has been rationalised [21a] in terms of the greater resonance stabilisation of the transition state derived from the *trans*-form.

In the light of these results it was of interest to determine the relative reactivity in addition to phenanthrene, which is closely related to the stilbenes. Theoretical calculations predict that positions 9 and 10 should have the highest reactivity towards free radicals,[23] and Levy and Szwarc [24] have measured the overall relative reactivity of phenanthrene in its reaction with methyl radicals while that towards trichloromethyl radicals has been measured by Kooyman and Farenhorst.[25] In neither case was a product isolated or the position of attack determined. It has been shown in the present investigation that subjection of the product of the radical-induced reaction of bromotrichloromethane with phenanthrene to our standard work-up procedure of dehydrobromination and hydrolysis gives rise to phenanthrene-9-carboxylic acid, thus providing the first demonstration of attack by alkyl radicals at the 9,10-double bond.

[15] Israelashvili and Shabatay, *J.*, 1951, 3261.
[16] Bevington and Brooks, *Makromol. Chem.*, 1958, **28**, 173.
[17] Wacholtz, *Z. phys. Chem.*, 1927, **125**, 1.
[18] Steinmetz and Noyes, *J. Amer. Chem. Soc.*, 1952, **74**, 4141.
[19] Kharasch, Mansfield, and Mayo, *J. Amer. Chem. Soc.*, 1937, **59**, 1155; Urushibara and Simamura, *Bull. Chem. Soc. Japan*, 1937, **12**, 507; 1938, **13**, 566.
[20] Skell and Woodworth, *J. Amer. Chem. Soc.*, 1955, **77**, 4638.
[21] (a) Bader, Buckley, Leavitt, and Szwarc, *J. Amer. Chem. Soc.*, 1957, **79**, 5621; (b) Matsuoka and Szwarc, *ibid.*, 1961, **83**, 1260.
[22] Lewis and Mayo, *J. Amer. Chem. Soc.*, 1948, **70**, 1533.
[23] Coulson, *J.*, 1955, 1435.
[24] Levy and Szwarc, *J. Chem. Phys.*, 1954, **22**, 1621; *J. Amer. Chem. Soc.*, 1955, **77**, 1949.
[25] Kooyman and Farenhorst, *Trans. Faraday Soc.*, 1953, **49**, 58.

Reaction of a trichloromethyl radical with *trans*- or *cis*-stilbene destroys the olefinic double bond and is energetically viable as a result of resonance stabilisation of the resulting benzyl-type radical (V ←→ VI). A similar situation obtains in reaction with


phenanthrene, but in this case the decrease in energy due to stabilisation of the inter-mediate radical must be offset against the energy required to disrupt the aromatic system, and this is reflected in the low value (0·18) of the reactivity of phenanthrene relative to *trans*-stilbene. This figure is in excellent agreement with that derived from the corresponding reaction of methyl radicals (0·15),[24] but differs from that (0·02) determined for attack of trichloromethyl radicals by Kooyman and Farenhorst.[25] The significance of the latter figure is, however, not great as a result of the method of its derivation, which involved measurement of the inhibitive effect of various hydrocarbons on the radical-induced addition of carbon tetrachloride to hexadecene or of bromotrichloromethane to styrene. The mechanism of inhibition is assumed to be the reaction of the trichloromethyl radical with the inhibitor to give an unreactive radical incapable of initiating new chains. This can be criticised on the grounds that the inhibitor may be attacked by radicals derived from the initiator and also that the secondary radicals formed by trichloromethyl attack on the inhibitor might be capable of initiating new chains. In this connection it is noteworthy that (*a*) products derived from reaction of t-butoxy-radicals, the initiator, with the olefin are formed in the peroxide-initiated reaction of bromotrichloromethane and *trans*-stilbene,[4] and (*b*) that the 1 : 1 adducts (or products derived from them) of the halide and olefin have been isolated from the latter reaction and also from the related reaction with phenanthrene as described above.

With regard to the addition of trichloromethyl radicals to substituted stilbenes it was concluded earlier [1] that the factor which mainly governs the orientation of addition is the relative stability of the possible intermediate radicals, *i.e.*, for *trans*-4-nitrostilbene addition proceeds by way of the radical (VII) which has greater possibilities of resonance stabilisation than radical (VIII).

It was further concluded that the additional stabilisation provided by conjugation with the 4-nitro- and other 4-substituents was small, and that the major stabilisation was that due to the benzyl-type radical. Since both possible intermediate radicals are of this type differences in reactivity between the olefinic carbon atoms are small.

These conclusions are confirmed by the magnitude of the relative rate ratios of *trans*-4-nitro- and *trans*-4,4'-dibromo-stilbene, and *trans*-β-2-naphthylstyrene. It is clear that the polarity of the substituent group has no effect on the overall reactivity of the olefinic double bond in the stilbene series. It is also noteworthy that the presence of nitromethane, a solvent of high dielectric constant, in the reaction does not significantly affect the relative ratio obtained for *trans*-4,4'-dibromostilbene.
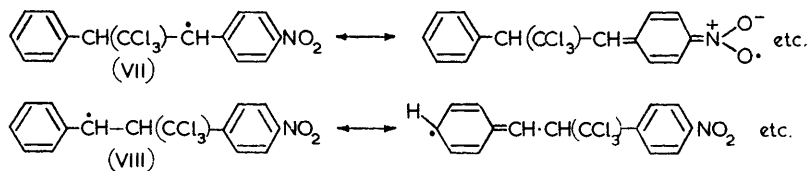

These observations can be rationalised in terms of the stability of the intermediate radicals in each case. The reactivities of *trans*-4-nitro- and *trans*-4,4'-dibromo-stilbene are similar to that of *trans*-stilbene, reflecting once again the small effects of the nitro-group

and bromine atom in the 4-position on the stability of the intermediate free radical (*e.g.*, VII).

The effect is most marked with *trans*-β-2-naphthylstyrene, in which case the relative rate ratio is 3·2. In this case additional resonance stabilisation can occur in one of the possible intermediate radicals (IX) thus explaining the higher reactivity of this olefin. It is thus predictable that radical addition to the parent olefin would occur mainly at the position α to the phenyl group, but the relevant experimental evidence is not yet available.
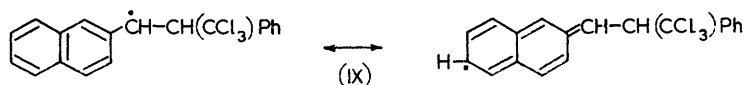
The products isolated from competition experiments involving *trans*-4-methylstilbene were found to be semi-solids and the reactivity ratios were not consistent, indicating that side reactions had occurred in this case, thus making the desired rate ratio of little significance. A similar effect was apparent in competitive reactions with *trans*-3,5-dimethylstilbene, where the amount of olefin consumed during the reaction, based on the acid titre, was greater than theoretical. These anomalous results are attributed to inter-action of trichloromethyl radicals with the side-chain methyl groups to give a substituted benzyl bromide by way of a substituted benzyl radical, thus:

$$Ar \cdot CH_3 + \cdot CCl_3 \longrightarrow Ar \cdot CH_2 \cdot \xrightarrow{CBrCl_3} Ar \cdot CH_2Br + \cdot CCl_3$$
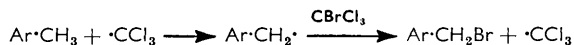
In the case of 4-methylstilbene the reaction might be expected to be facilitated as a result of the high stability of the resulting benzyl radical (X). The standard working-up
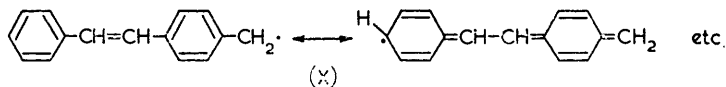
of mixtures containing such products would lead to contamination of the final mixture of acids to an unknown extent. This radical-chain process has been shown to occur under initiation by ultraviolet light,[26] but it is difficult to assess the extent with which it would compete with addition to the double bond. Our experimental results suggest that it is not negligible.

trans-β-Methylstyrene differs from other olefins studied in this investigation in that a benzyl-type radical is formed only by radical addition to the β-carbon atom. This no doubt explains why the adduct $Ph \cdot CHBr \cdot CH(CCl_3) \cdot CH_3$ is formed almost exclusively.[27] Discussion of the observed reactivity of this olefin is, however, deferred to a subsequent paper in which relative rates of attack of free radicals on substituted olefins of the type $Ph \cdot CH\colon CHX$ and $X \cdot CH\colon CHY$, where X and Y are groups other than aryl, will be discussed.

[26] Huyser, *J. Amer. Chem. Soc.*, 1960, **82**, 391.
[27] Cadogan, unpublished observation.