805. *Quantitative Aspects of Radical Addition. Part I. The Addition of Bromotrichloromethane to* cis- *and* trans-*Stilbene.*

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The free-radical addition of bromotrichloromethane to *cis*- and *trans*-stilbene has been studied and mechanisms of initiation of the addition to *trans*-stilbene induced by di-t-butyl peroxide have been established. The additions proceed by way of 1,2-diphenyl-3,3,3-trichloropropyl radicals which react stereospecifically with bromotrichloromethane to give the 1 : 1 adduct, *i.e.*, that consisting of one molecule of the halide and one of stilbene. Quantitative conversion of this adduct into α-phenyl-*trans*-cinnamic acid has been achieved and its application to the quantitative study of free-radical addition of bromotrichloromethane to substituted stilbenes is indicated.

In free-radical addition to olefins $R\cdot CH{:}CH_2$ the point of initial attack is exclusively the terminal $:CH_2$ group. This specificity, which is remarkable in view of the homolytic nature of the reaction, has been generally explained on the basis of the greater stability of the intermediate radical $\cdot CRH\cdot CH_2X$, formed by addition of a radical $X\cdot$ to $R\cdot CH{:}CH_2$, than of $R\cdot CHX\cdot CH_2\cdot$; polar and steric factors have been considered to be less important (cf. Cadogan and Hey[1]). Fewer data are available concerning free-radical addition of non-terminal olefins $R^1R^2C{:}CR^3R^4$; Huang[2] has obtained an order of the relative stabilising effects of various substituents on the stability of the intermediate radicals obtained from such olefins. Unfortunately, few of these systems were capable of quantitative resolution. The absence of such quantitative data is characteristic of this field and it was to meet this situation that the work to be described in this and subsequent papers was undertaken.

It was our aim to study free-radical addition of *cis*- and *trans*-substituted stilbenes (I) quantitatively. It was hoped that results with 3- and 4-substituted compounds would afford a correlation between the relative reactivities of the carbon atoms of the olefinic double bond and the properties of substituent groups in the nucleus. In order to give the necessary quantitative results, (*a*) the system must give, preferably in a non-reversible process, a high yield of 1 : 1 adduct, *i.e.*, that consisting of one molecule of the addendum XY and one molecule of stilbene, and a negligible yield of 1 : 2 adducts and other telomers, and (*b*) the expected mixture of adducts (II) and (III) should be stable, not interconvertible, and capable of being analysed quantitatively.

$$\underset{\text{(I)}}{Ar{\cdot}CH{:}CHAr'} \qquad \underset{\text{(II)}}{Ar{\cdot}CHX{\cdot}CHY{\cdot}Ar'} \qquad \underset{\text{(III)}}{Ar{\cdot}CHY{\cdot}CHX{\cdot}Ar'}$$

Very few radical additions to *cis*- and *trans*-stilbene have been reported. Szwarc and his co-workers[3] measured ethyl and methyl affinities of these compounds but did not isolate any products. Stevens,[4] and Schechter and his co-workers,[5] investigated the addition of dinitrogen tetroxide to these olefins under free-radical conditions, but none of these systems was suitable for our purpose. Undoubtedly, the reagent which best satisfied requirement (*a*) is bromotrichloromethane, which gives high yields of 1 : 1 adduct[1] and was therefore the reagent of our choice. Addition of this to substituted stilbenes has not been reported but would be expected to give either or both of the adducts (II) and (III) ($X = CCl_3$, $Y = Br$). Analysis of this mixture, directly or after quantitative conversion into suitable derivatives, *e.g.*, the substituted α-phenylcinnamic acids which could be analysed by ultraviolet spectrography, would then give a measure of the directing influences of the substituent on addition to the olefinic double bond.

$$CCl_3{\cdot}CHAr{\cdot}CHBrAr' \xrightarrow{-\,HBr} CCl_3{\cdot}CAr{:}CHAr' \longrightarrow HO_2C{\cdot}CAr{:}CHAr'$$

Free-radical addition of bromotrichloromethane to *trans*-stilbene has now been shown to give 1-bromo-3,3,3-trichloro-1,2-diphenylpropane (IV) after initiation by dibenzoyl peroxide, di-t-butyl peroxide, or ultraviolet light. The same product (IV) is obtained from both the light- and peroxide-induced reactions of *cis*-stilbene. Thus the same intermediate radical (V) is formed in each case and the reaction resembles to some extent the free-radical addition of bromotrichloromethane to *cis*- and *trans*-but-2-ene, which is not stereospecific and is irreversible.[6]

$$\text{(IV)}\ \ CCl_3{\cdot}CHPh{\text -}CHBrPh \qquad CCl_3{\cdot}CHPh{\cdot}CHPh{\cdot}\ \ \text{(V)}$$

Addition of a trichloromethyl radical to *trans*-stilbene will give equal amounts of the intermediate radicals (VI) and (VII), which in theory would be expected to reach equilibrium between their conformers by inversion before abstraction of a bromine atom from the chain-transfer reagent, bromotrichloromethane, and thus give rise to four isomeric

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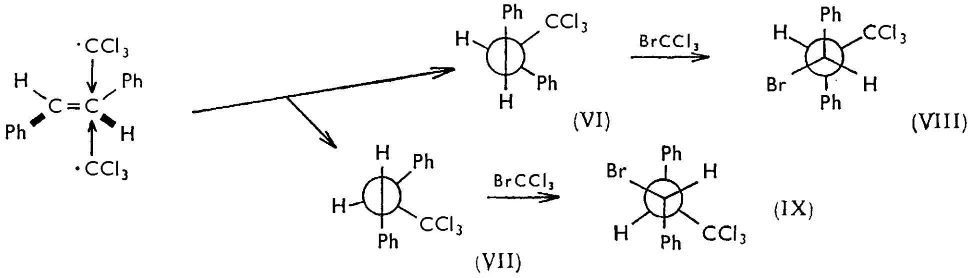
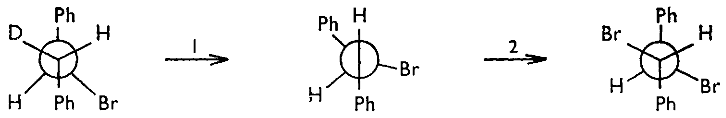
[1] Cadogan and Hey, *Quart. Rev.*, 1954, **8**, 308.
[2] Huang, *J.*, 1956, 1749; 1957, 1342.
[3] Szwarc *et al.*, *J. Amer. Chem. Soc.*, 1956, **78**, 3590, 3320; 1957, **79**, 5621.
[4] Stevens, *J. Amer. Chem. Soc.*, 1959, **81**, 3593.
[5] Gardikes, Pagano, and Schechter, *Chem. and Ind.*, 1958, 632.
[6] Skell and Woodworth, *J. Amer. Chem. Soc.*, 1955, **77**, 4638.

1 : 1 adducts distributed between two different enantiomorphic pairs. In accord with this Skell and Woodworth[6] isolated the same mixture of diastereoisomers from the products of the reactions of bromotrichloromethane with the but-2-enes. In contrast, we were able to detect only one racemic 1 : 1 adduct to the stilbenes. This suggests that the chain-transfer reactions of the intermediate radicals (VI) and (VII) are stereospecific, proceeding through preferred conformations in which the bulky phenyl and trichloromethyl groups are as far apart as possible. It is thus reasonable that the bromotrichloromethane molecule should approach the radicals from the least hindered side in each case, to give a single racemic mixture of isomeric 1 : 1 adducts (VIII) and (IX).



The isolation of the same adduct from both *cis*- and *trans*-stilbene may in this case be due to isomerisation of the *cis*-isomer before reaction with trichloromethyl radicals. Unpublished work by Dr. P. W. Inward indicates, however, that in reactions of *cis*-stilbene with bromotrichloromethane induced by di-t-butyl peroxide very little isomerisation occurs before addition of trichloromethyl radicals, in which case application of the above argument also leads to the conclusion that the product should be identical with that obtained from *trans*-stilbene, as observed.

A similar rationalisation has been put forward by Greene, Remers, and Wilson,[7] who observed that free-radical chain bromination with *N*-bromosuccinimide of *erythro*-α-bromo-β-deuterobibenzyl (CHDPh·CHBrPh) gave the *meso*-dibromide, and that removal of deuterium atoms from the substrate occurred nearly twice as rapidly as that of hydrogen atoms. They inferred that this reversal of the usual isotope effect was partially a steric phenomenon involving preferred conformations of both bromide and the resulting intermediate radical, which is very similar to that involved in the radical-chain addition of bromotrichloromethane to *cis*- and *trans*-stilbene.



1, $[CH_2 \cdot CO]_2 > N\cdot$. 2, $[CH_2 \cdot CO]_2 > NBr$.

Conversion of the 1 : 1 *Adduct into α-Phenyl-*trans*-cinnamic Acid.*—One-stage conversion of the adduct (IV) into α-phenyl-*trans*-cinnamic acid by means of aqueous or aqueous-ethanolic alkali was only partially successful, as was the use of triethylamine as a dehydrobrominating agent followed by hydrolysis with ethanolic alkali. Reaction of the adduct with ethanolic potassium hydroxide gave a product formulated as 1,1-dichloro-3-ethoxy-2,3-diphenylprop-1-ene (X), presumably formed by substitution of benzylic bromine by ethoxide followed by elimination of hydrogen chloride. This dichloride, on treatment with perchloric acid in acetic acid, gave α-phenyl-*trans*-cinnamic acid, but the overall yield (85%) in this reaction was unsatisfactory. Holysz[8] in 1953 reported that reaction

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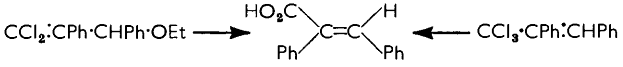
[7] Greene, Remers, and Wilson, *J. Amer. Chem. Soc.*, 1957, **79**, 1416.
[8] Holysz, *J. Amer. Chem. Soc.*, 1953, **75**, 4432.

of a 4-bromo-3-oxo-steroid with anhydrous lithium chloride in dimethylformamide led to some dehydrobromination rather than replacement by chloride. Application of this method to our system gave an excellent yield (98%) of α-trichloromethylstilbene (XI), which on hydrolysis with perchloric acid in acetic acid was quantitatively converted into α-phenyl-*trans*-cinnamic acid. This result has no stereochemical significance because the isomeric *cis*-cinnamic acid is isomerised to the *trans*-isomer under the conditions of the carboxylation.



(X) (XI)

Mechanisms of Initiation and Termination of the Addition induced by Di-t-butyl Peroxide.—The experiments involving di-t-butyl peroxide were carried out at 105° for 72 hr. with a halide : stilbene ratio of 11 : 1. At this temperature decomposition of the peroxide is slow,[9] so relatively large amounts of peroxide (0·2—0·5 mole per mole of olefin) were used. Under these conditions good conversions into the 1 : 1 adduct were obtained relatively quickly without the formation of telomers. A reduction of the ratio of halide to olefin produced a more efficient radical chain, and disproportionally less peroxide was required for a high yield of adduct. In most free-radical chain additions, and those involving bromotrichloromethane in particular, the average chain lengths are very large,[1] and consequently the proportions of groupings or products derived from the initiators are very small; hence no work concerning the initiation of reactions involving bromotrichloromethane has been reported, although it is generally assumed that initiation reactions of the following type occur:

$$\text{Peroxide} \longrightarrow 2\text{X}\cdot$$

$$\text{X}\cdot + \text{BrCCl}_3 \longrightarrow \text{XBr} + \cdot\text{CCl}_3\text{, etc.}$$

The use in our experiments of larger amounts of initiator has led us to search for the products of decomposition of di-t-butyl peroxide in the presence of bromotrichloromethane and *trans*-stilbene. Those products which co-distilled with bromotrichloromethane were identified and estimated by gas–liquid chromatography, while the residue was divided into two portions, one of which was resolved by distillation and the other by dehydrobromination and hydrolysis to α-phenyl-*trans*-cinnamic acid and chromatography of the neutral fraction. The results summarised in the Table indicate that a significant quantity of trichloromethyl radicals, which can initiate the chain reaction, is formed by displacement by a free t-butoxy-radical on bromotrichloromethane to give t-butyl hypobromite (equation iv) and that chain termination occurs by dimerisation of trichloromethyl radicals to give hexachloroethane, although the recovery of the latter was low.

Addition of bromotrichloromethane to *trans*-stilbene induced by di-t-butyl peroxide.

	Volatile products (mole/mole of peroxide)		Volatile products (moles/mole of stilbene)	
			method (*a*) *	method (*b*) *
$Me_3C\cdot OBr$	1·3	$CHPhBr\cdot CHPh\cdot CCl_3$	0·84	—
Me_3CBr	0·13	CHPh:CHPh	0·09	0·08
C_2Cl_6	0·15	$Ph\cdot CO\cdot CH_2Ph$	0·05	0·07
		$CHPh:CPh\cdot CO_2H$	—	0·83

* See Experimental section.

The formation of equivalent amounts of t-butyl bromide and deoxybenzoin suggests

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[9] Raley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 1336.

that a second mode of initiation is also operative. It is well known [10] that decomposition of di-t-butyl peroxide does not normally lead to the formation of t-butyl radicals; hence the formation of t-butyl bromide in our case is unlikely to be the result of simple abstraction of a bromine atom from the solvent. Frey [11] has shown that some of the products of photolysis of di-t-butyl peroxide can be explained by assuming the formation of free t-butyl radicals, but these special conditions did not obtain in our case. Further, t-butyl bromide is not formed in the reaction of di-t-butyl peroxide with bromotrichloromethane in the absence of *trans*-stilbene. A possible rationalisation involves reaction of a t-butoxy-radical as in (vi) and (viii), to give 1-bromo-1,2-diphenyl-2-t-butoxyethane (XIII). Rearrangement of the latter could then give t-butyl bromide and deoxybenzoin. This would, however, involve an S_N2-type attack on the t-butyl group, which is unlikely; further we were unable to obtain direct evidence of this mechanism by independent preparation and decomposition of the bromide (XIII). On the other hand, the corresponding methoxy-compound decomposed, when heated, into deoxybenzoin, *trans*-stilbene, and stilbene dibromide. In this case, however, a different mechanism may be involved. Alternatively, the intermediate radical (XII) may react by rearrangement to give a t-butyl radical and hence t-butyl bromide. Here again, however, there are no precedents and we have no direct evidence.

Chain initiation

$$Me_3C{\cdot}O{\cdot}O{\cdot}CMe_3 \longrightarrow 2Me_3C{\cdot}O{\cdot} \qquad \text{(iii)}$$

$$Me_3C{\cdot}O{\cdot} + BrCCl_3 \longrightarrow Me_3C{\cdot}OBr + {\cdot}CCl_3 \qquad \text{(iv)}$$

$$ {\cdot}CCl_3 + CHPh{:}CHPh \longrightarrow CCl_3{\cdot}CHPh{\cdot}CHPh{\cdot} \qquad \text{(v)}$$

$$Me_3C{\cdot}O{\cdot} + CHPh{:}CHPh \longrightarrow CMe_3{\cdot}O{\cdot}CHPh{\cdot}CHPh{\cdot}\ \text{(XII)} \qquad \text{(vi)}$$

Chain propagation

$$CCl_3{\cdot}CHPh{\cdot}CHPh{\cdot} + BrCCl_3 \longrightarrow Ph{\cdot}CH(CCl_3){\cdot}CHBr{\cdot}Ph + {\cdot}CCl_3 \qquad \text{(vii)}$$

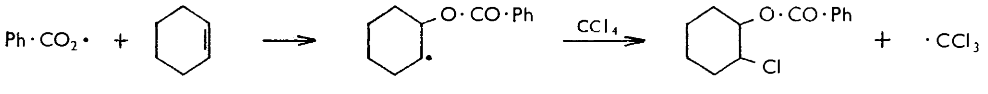
$$CMe_3{\cdot}O{\cdot}CHPh{\cdot}CHPh{\cdot} + BrCCl_3 \longrightarrow CMe_3{\cdot}O{\cdot}CHPh{\cdot}CHPhBr\ \text{(XIII)} + {\cdot}CCl_3 \qquad \text{(viii)}$$

Chain termination

$$2{\cdot}CCl_3 \longrightarrow C_2Cl_6 \qquad \text{(ix)}$$

$$CMe_3{\cdot}O{\cdot}CHPh{\cdot}CHPhBr \longrightarrow Ph{\cdot}CO{\cdot}CH_2Ph + Me_3CBr \qquad \text{(x)}$$

The predominance of chain initiation by abstraction of a bromine atom by the primary product of decomposition of the peroxide, the t-butoxy-radical [equation (iv)], over that involving addition of this radical to *trans*-stilbene [equation (vi)] is the reverse of that observed by Kooyman and Farenhorst,[12] who showed that the benzoyl peroxide used to initiate the addition of carbon tetrachloride to cyclohexene appears largely (55%) as 2-chlorocyclohexyl benzoate, thus indicating that the main initiation mechanism is one of addition, as follows:



That chain initiation by the abstraction mechanism $Ph{\cdot} + CCl_4 \longrightarrow PhCl + {\cdot}CCl_3$ is relatively unimportant is shown by the appearance of only 10% of the phenyl radicals as chlorobenzene and 12% as benzoic acid. The differences between these reactions and those reported in this paper are probably due to two factors: (*a*) the abstraction of a bromine atom from bromotrichloromethane is a favoured reaction, and (*b*) the concentration of olefin is much lower in our experiments.

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[10] See, for example, McMillan and Wijnen, *Canad. J. Chem.*, 1958, **36**, 1227.
[11] Frey, *Proc. Chem. Soc.*, 1959, 385.
[12] Kooyman and Farenhorst, *Rec. Trav. chim.*, 1951, **70**, 867.

Having thus established the course of the peroxide-induced reaction of bromotrichloromethane with *trans*-stilbene and the method of accurate estimation of the amount of addition by conversion into α-phenyl-*trans*-cinnamic acid, we then made quantitative experiments involving substituted stilbenes and related olefins. The results of these experiments, which are concerned with (i) the directive effects of substituents as measured by the ratios of isomerides (II) and (III), (ii) the overall activation or deactivation of the double bond compared with *trans*-stilbene as a standard, and (iii) the effect of solvents on these reactions, will be presented in subsequent papers.

EXPERIMENTAL

Chromatographic separations were carried out on activated alumina (Peter Spence and Sons Ltd.; type " H "). Gas–liquid chromatography was carried out with a Perkin–Elmer " Fraktometer," model 116.

Bromotrichloromethane (Eastman Kodak) was dried ($MgSO_4$) and fractionally distilled through a 4-ft. Fenske column packed with helices and fitted with a still-head of the total-reflux partial take-off type. The apparatus was protected from light. The product had b. p. 103·5°, n_D^{20} 1·5061, and contained carbon tetrachloride (2½% w/w, determined by gas–liquid chromatography as described below). The sample used for the " initiation–termination " experiments (see below) was refractionated several times to give material of b. p. 103·5°, n_D^{20} 1·5061, which contained 0·38% w/w of carbon tetrachloride.

NN-Dimethylformamide, b. p. 153°, purified by the method of Thomas and Roctron,[13] was stored over $MgSO_4$.

Preparation of Stilbenes.—*trans*-Stilbene (B.D.H.) was crystallised to constant m. p. (124·5—125°) from ethanol. α-Phenyl-*trans*-cinnamic acid, crystallised from aqueous ethanol and of m. p. 172·5°, was prepared by Buckles and Bremer's method [14] (Found: C, 80·4; H, 5·5. Calc. for $C_{15}H_{12}O_2$: C, 80·4; H, 5·4%). t-Butyl bromide, b. p. 70—71°, n_D^{25} 1·4232, was prepared by Bryce-Smith and Howlett's method; [15] they reported b. p. 73°, n_D^{25} 1·4249. Deoxybenzoin, prepared by Kohler and Nygaard's method,[16] was recrystallised to constant m. p. (55—56°) from methanol; Allen and Barker [17] reported m. p. 55—56°. *cis*-Stilbene was prepared by catalytic decomposition of α-phenyl-*trans*-cinnamic acid as follows: a solution of the acid (23 g.), in boiling technical quinoline (80 ml.), was treated with copper chromite (2 g.) prepared by Adkins and Connor's method; [18] after 1½ hr. the product was poured into 10% hydrochloric acid (500 ml.) and extracted with ether (5 × 100 ml.); after filtration, the ether extracts were washed with aqueous sodium hydrogen carbonate and dried ($MgSO_4$); distillation left a residue which, on trituration with hexane, deposited no *trans*-stilbene; the residue was distilled, to give *cis*-stilbene (11·8 g.), b. p. 82—83°/10^{-2} mm., n_D^{21} 1·6209 (Buckles and Wheeler [19] reported n_D^{20} 1·6212).

Di-t-butyl peroxide was dried ($MgSO_4$) and distilled; it had b. p. 108°, n_D^{25} 1·3858. The gas–liquid chromatogram indicated the absence of impurities.

Professor D. H. Hey, F.R.S., is thanked for a sample of hexachloroethane, m. p. 185°.

t-Butyl Hypobromite.—The preparation of pure t-butyl hypobromite has not been reported, although Anbar and Dostrovsky [20] reported, without experimental details, the preparation of a solution of the hypobromite in carbon tetrachloride. Our method, based on that of Anbar and Dostrovsky, is as follows: t-butyl alcohol (15 g.) in carbon tetrachloride (30 g.) was shaken with aqueous hypobromous acid prepared as described by Derbyshire and Waters.[21] The carbon tetrachloride solution was separated, washed with 10% aqueous sodium carbonate

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[13] Thomas and Roctron, *J. Amer. Chem. Soc.*, 1957, **79**, 1843.
[14] Buckles and Bremer, *Org. Synth.*, 1953, **33**, 70.
[15] Bryce-Smith and Howlett, *J.*, 1951, 1141.
[16] Kohler and Nygaard, *J. Amer. Chem. Soc.*, 1930, **52**, 4128.
[17] Allen and Barker, *Org. Synth.*, 1943, Coll. Vol. II, p. 156.
[18] Adkins and Conner, *J. Amer. Chem. Soc.*, 1931, **53**, 1091.
[19] Buckles and Wheeler, *Org. Synth.*, 1953, **33**, 88.
[20] Anbar and Dostrovsky, *J.*, 1954, 1108.
[21] Derbyshire and Waters, *J.*, 1950, 571.

until acid-free, and dried ($MgSO_4$). This solution of t-butyl hypobromite was stored in a dark bottle. Iodometric analysis of the solution indicated 47·0% w/w of t-butyl hypobromite. Gas–liquid chromatography (see below) of the mixture indicated the presence of one component other than carbon tetrachloride; on the assumption that this was t-butyl hypobromite the composition of the mixture was: CCl_4 53·7%, t-C_4H_9·OBr 46·3% (by weight).

Addition of Bromotrichloromethane to trans-*Stilbene*.—(i) *In the presence of dibenzoyl peroxide.* Dibenzoyl peroxide (1·2 g., 0·005 mole) was added in six portions, in 2 hr., to *trans*-stilbene (8 g., 0·04 mole) in bromotrichloromethane (70 g., 0·35 mole) at 80°. After 72 hr., the brown mixture was extracted with sodium hydrogen carbonate and dried. The alkaline washing gave no benzoic acid on acidification. The organic solution, after filtration was distilled to leave a crystalline residue (11·42 g.) which was distilled, giving *trans*-stilbene (2·21 g., 28%), b. p. 116—120°/10^{-2} mm., m. p. and mixed m. p. 119—120° (Found: C, 93·2; H, 6·7. Calc. for $C_{14}H_{12}$: C, 93·3; H, 6·7%), and a yellow solid (8·20 g., 67%), b. p. 140—145°/10^{-2} mm., m. p. 98—100°). Recrystallisation of the latter from light petroleum and then ethanol gave 1-*bromo*-3,3,3-*trichloro*-1,2-*diphenylpropane* as colourless needles, m. p. 107—108° (mixed m. p. with *trans*-stilbene, 94—96°) (Found: C, 47·8; H, 3·2. $C_{15}H_{12}BrCl_3$ requires C, 47·6; H, 3·2%).

The use of different molar ratios of reactants (stilbene, 0·028; bromotrichloromethane, 0·2519; peroxide, 0·008 mole) gave *trans*-stilbene (22%) and 1-bromo-3,3,3-trichloro-1,2-diphenylpropane (74%; m. p. 107—107·5°).

(ii) *In the presence of di-t-butyl peroxide.* A mixture of *trans*-stilbene (0·028 mole), bromotrichloromethane (0·2519 mole) and di-t-butyl peroxide (0·008 mole) was boiled under reflux for 24 hr. Working up of the mixture, as described above, but without the alkaline washing, gave 1-bromo-3,3,3-trichloro-1,2-diphenylpropane (1 : 1 adduct) as a cream solid, which recrystallised from ethanol as needles (8·4 g., 80%), m. p, 107—108° alone and mixed with a sample from experiment (i).

(iii) *In the presence of ultraviolet radiation. trans*-Stilbene (2·000 g., 0·0111 mole) in bromotrichloromethane (24·26 g., 0·1222 mole) was boiled under reflux, under nitrogen, in a quartz flask illuminated by an ultraviolet lamp (125 w; 365 mμ) for 16 hr. The mixture was distilled under reduced pressure under nitrogen to remove the solvent. The residue (3·52 g.) was further distilled at 10^{-2} mm., giving: (*a*) a white sublimate (0·22 g.) of hexachloroethane, m. p. and mixed m. p. 182—185°; (*b*) *trans*-stilbene (0·88 g.), b. p. 118—120°, m. p. and mixed m. p. 123—124·5°; (*c*) 1-bromo-3,3,3-trichloro-1,2-diphenylpropane (2·17 g.), b. p. 138—142°, m. p. 105—106°, mixed m. p. 106—107°; and (*d*) a solid (0·13 g.) which sublimed. Recrystallisation from ethanol of fraction (*d*) gave needles, m. p. and mixed m. p. 231—231·5° (decomp.), of 1,2-dibromo-1,2-diphenylethane.

Addition of Bromotrichloromethane to cis-*Stilbene*.—(i) *In the presence of di-t-butyl peroxide.* Di-t-butyl peroxide (0·0028 mole) was added to a mixture of *cis*-stilbene (0·0056 mole) and bromotrichloromethane (0·0611 mole) kept at 105°. The reaction was allowed to proceed for 3 days under nitrogen. The excess of solvent was removed at 20 mm. and the residual yellow syrup (2·41 g.) was distilled at 10^{-2} mm., giving (*a*) a sublimate (0·25 g.) of hexachloroethane, m. p. and mixed m. p. 183—185°, and 1-bromo-3,3,3-trichloro-1,2-diphenylpropane (2·05 g., 98%), b. p. 140—142°, m. p. and mixed m. p. 107—108° after recrystallisation. No *trans*-stilbene was detected.

(ii) *In the presence of ultraviolet radiation.* The experiment was conducted under the same conditions, and with the same quantities, as described above for the *trans*-isomer; the following products were obtained: hexachloroethane (0·55 g.), m. p. and mixed m. p. 182—184°; *trans*-stilbene (0·60 g., 30%), m. p. and mixed m. p. 124—124·5°); 1-bromo-3,3,3-trichloro-1,2-diphenylpropane (2·27 g.), m. p. 106—108°, mixed m. p. 107—108°; and 1,2-dibromo-1,2-diphenylethane (0·38 g.), m. p. and mixed m. p. 230—230·5°.

Conversion of 1-*Bromo*-3,3,3-*trichloro*-1,2-*diphenylpropane into* α-*Phenyl*-trans-*cinnamic Acid*.—(*i*) *By the use of* 10% *alcoholic potassium hydroxide.* The 1 : 1 adduct (0·5 g.) in ethanol (40 ml.) with an excess of 10% aqueous potassium hydroxide (35 ml.) was boiled under reflux for 24 hr. The alkaline solution was treated to remove silicic acid as follows: The boiling solution was acidified, then basified with sodium hydrogen carbonate and boiled to coagulate the precipitated silicic acid which was removed by filtration while hot. The cooled filtrate was extracted with ether (4 × 30 ml.) and acidified, the acid solution was extracted with methylene chloride (5 × 30 ml.), and the extracts were dried ($CaCl_2$). Evaporation of the filtered methylene chloride left α-phenyl-*trans*-cinnamic acid (0·09 g., 33%), m. p. 167—170°. Recrystallisation from ethanol–water (3 : 2 v/v) gave the pure acid, m. p. and mixed m. p. 171—172·5° (Found: C, 79·8; H, 5·4. Calc. for $C_{15}H_{12}O_2$: C, 80·4; H, 5·4%).

Thus dehydrobromination of the adduct had occurred, followed by hydrolysis.

Treatment of the 1 : 1 adduct with 10% or 40% aqueous sodium hydroxide resulted in no reaction. Treatment with alcoholic 15% potassium hydroxide gave a low (24%) yield of α-phenyl-*trans*-cinnamic acid. Dehydrohalogenation and hydrolysis as a one-stage process was therefore unsatisfactory for quantitative work.

(ii) *By the use of triethylamine followed by alcoholic* 10% *potassium hydroxide.* The 1 : 1 adduct (2·0 g.) was allowed to react with triethylamine (40 ml.) at room temperature for 24 hr. After filtration the excess of base was removed by distillation and the residue was boiled under reflux with ethanolic 10% potassium hydroxide for 36 hr. Working up, as described above, gave α-phenyl-*trans*-cinnamic acid (0·85 g., 70%), m. p. and mixed m. p. 169—171°.

Dehydrohalogenation of 1-*Bromo*-3,3,3-*trichloro*-1,2-*diphenylpropane*.—(i) *By the use of ethanolic potassium hydroxide.* The 1 : 1 adduct (3·0 g.; 0·0077 mole) and potassium hydroxide (1·6 g.) in ethanol (80 ml.) were boiled under reflux for a few minutes and left at room temperature for 2 hr., ethanol was removed, the residue was diluted with water, extracted into chloroform, and the extracts were washed with sodium hydrogen carbonate and dried ($MgSO_4$). No acid was obtained from the alkaline washings. Removal of the chloroform and distillation of the residue (1·92 g.) gave crystals (1·88 g.), b. p. 106—108°/10^{-2} mm., m. p. 39—39·5° (Found: C, 66·6; H, 5·2; Cl, 23·1. $C_{17}H_{16}Cl_2O$ requires C, 66·6; H, 5·2; Cl, 23·2%). The product was assumed to be 1,1-*dichloro*-3-*ethoxy*-2,3-*diphenylprop*-1-*ene.*

(ii) *By the use of anhydrous lithium chloride in* NN-*dimethylformamide.* Lithium chloride ("AnalaR") was heated over a Bunsen flame for 1 hr. and allowed to cool in a desiccator. The 1 : 1 adduct (1·0 g., 0·0026 mole), dissolved in the minimum amount (6 ml.) of *NN*-dimethylformamide, and anhydrous lithium chloride (0·44 g.; 0·0104 mole) were heated on a steam-bath under nitrogen for 4 hr. The mixture was diluted with water (10 ml.), and the solid which separated was collected, washed with water, and dried, to give α-*trichloromethylstilbene* (0·785 g.; 98%), m. p. 74—75°. Recrystallisation from light petroleum (b. p. 40—60°) gave needles, m. p. 75—75·5° (Found: C, 60·6; H, 3·9; Cl, 34·7. $C_{15}H_{11}Cl_3$ requires C, 60·5; H, 3·7; Cl, 35·8%).

Hydrolysis of α-Trichloromethylstilbene.—The stilbene (1·0 g.) and 60% perchloric acid (1·0 ml.) in acetic acid (25 ml.) were boiled under reflux until the evolution of hydrochloric acid had ceased (8 hr.). Removal of the excess of acetic acid at 20 mm. left a solid (0·75 g.) which was dissolved in benzene (20 ml.) and extracted with saturated sodium hydrogen carbonate (12 × 10 ml.). The combined alkaline washings were washed with benzene and boiled. The cooled solution was acidified to pH 2—3 with concentrated hydrochloric acid, the product was extracted into methylene chloride (5 × 10 ml.), and the extracts were dried (Na_2SO_4). Evaporation of the filtered solution left α-phenyl-*trans*-cinnamic acid (0·751 g., 100%), m. p. and mixed m. p. 172—172·5°.

Hydrolysis of 1,1-*Dichloro*-3-*ethoxy*-2,3-*diphenylprop*-1-*ene*.—The dichloride, on treatment with perchloric acid in acetic acid as described above, gave α-phenyl-*trans*-cinnamic acid (90%), m. p. and mixed m. p. 172°.

Hydrolysis of Hexachloroethane.—Hexachloroethane was unaffected by treatment with perchloric acid in acetic acid under the above conditions.

Stability of 1-*Bromo*-3,3,3-*trichloro*-1,2-*diphenylpropane*.—The bromide was unchanged after storage at 105° for 72 hr. under nitrogen, or irradiation by ultraviolet light in acetone solution or the solid state.

*Stability of α-Phenyl-*cis*-cinnamic Acid in the Carboxylation Reaction.*—The acid (0·45 g.) in acetic acid (20 ml.) and 60% perchloric acid (1 ml.) was treated with dry hydrogen chloride for 45 min. and boiled under reflux for 15 hr. The acid (0·443 g.; 98·5%) obtained in the usual way had m. p. 120—144°. Recrystallisation from aqueous ethanol gave α-phenyl-*trans*-cinnamic acid (0·132 g.), m. p. and mixed m. p. 170—174°.

Investigation of the Mechanisms of Chain Initiation and Termination in the Addition of Bromotrichloromethane to trans-*Stilbene in the Presence of Di-t-butyl Peroxide.*—Di-t-butyl peroxide (4 g.; 0·0274 mole) was added to a solution of *trans*-stilbene (10 g., 0·0556 mole) in bromotrichloromethane (121·3 g.; 0·611 mole) which had been saturated with nitrogen, at 105°. After 72 hr. the yellow mixture was distilled under nitrogen through a darkened fractionating column (30 cm.) packed with Fenske helices and fitted with a still-head of the total-reflux partial take-off type. Three fractions were collected at a take-off ratio of 10 : 1, as follows: (*a*) 19·73 g., b. p. 90—95°; (*b*) 60·20 g., b. p. 98—104°; (*c*) 13·95 g., b. p. 104—106°. These fractions were analysed by gas–liquid chromatography as described below. The residue was made up to a standard volume (50·0 ml.) in acetone, a portion (25·0 ml.) evaporated to dryness, and the residue treated with *NN*-dimethylformamide (21 ml.) and lithium chloride (4·7 g.) as described above (method *b* in Table above). The dehydrobrominated product was then extracted into chloroform. After removal of the solvent it was hydrolysed by 60% perchloric acid (6 ml.) in acetic acid (50 ml.) as previously described. Working up of the acidic portion gave α-phenyl-*trans*-cinnamic acid (5·2151 g.), m. p. and mixed m. p. 172—172·5°. The neutral portion, in benzene, from the hydrolysis was evaporated to dryness and the residue (0·99 g.) was dissolved in light petroleum (b. p. 60—80°; 50 ml.) and chromatographed on alumina (25 × 1·5 cm.). Elution with light petroleum (b. p. 60—80°; 200 ml.) gave *trans*-stilbene (0·43 g.), m. p. and mixed m. p. 121—123°. Elution with benzene (200 ml.) gave deoxybenzoin (0·3884 g.), m. p. and mixed m. p. 50—54° (correct infrared spectrum).

The above results were confirmed by another method of working up of the remainder (25 ml.) of the acetone solution obtained above (method *a*): removal of the acetone left a residue (10·01 g.) which was distilled in apparatus described by Augood, Hey, and Williams [22] to give the following fractions: (*d*) hexachloroethane (0·3 g.), m. p. and mixed m. p. 183—184°; (*e*) a solid (0·81 g.), b. p. 115—120°/10^{-2} mm., which on recrystallisation from ethanol gave *trans*-stilbene (0·48 g.), m. p. and mixed m. p. 123—124°; evaporation of the mother-liquors and recrystallisation of the residue from methanol gave deoxybenzoin (0·30 g.), m. p. 50—55°, mixed m. p. 53—55° (correct infrared spectrum); (*f*) 1-bromo-3,3,3-trichloro-1,2-diphenylpropane (8·81 g.), b. p. 140—143°/10^{-2} mm. [recrystallisation from methanol gave needles (8·0 g.), m. p. and mixed m. p. 107—108°]; and (*g*) unidentified residue (0·006 g.), b. p. >220°/10^{-2} mm.

A control experiment in which bromotrichloromethane was kept at 105° under nitrogen for 3 days and worked up as described above, revealed (gas–liquid chromatography) that no thermal decomposition of the solvent had occurred.

A complementary experiment in which a mixture of hexachloroethane (0·6320 g.) and bromotrichloromethane (22·00 g.) was fractionally distilled under the conditions described above, revealed that hexachloroethane (0·1012 g.) co-distilled with the solvent. Analyses were by gas–liquid chromatography as described below.

Gas–Liquid Chromatography.—The fractions obtained from the first distillation of the reaction mixture in the preceding experiment were analysed as follows. Fraction (*a*) was shown by comparison with synthetic mixtures to contain the following components (retention times relative to carbon tetrachloride in parentheses): acetone (0·35), t-butyl alcohol (0·44), and an unidentified component (X) (0·50), t-butyl hypobromite (0·67), t-butyl bromide (0·75), carbon tetrachloride (1·00), and bromotrichloromethane (1·86). The column was a Perkin–Elmer 2-m. type " C " (silicone grease on Celite), used at 84° with a column pressure of 0·7 kg./cm.^{2} of nitrogen, with a detector voltage of 6·0. Considerable variation of temperature, column pressure, rate of flow of gas, and detector voltage did not alter the relative retention times. The above identification was confirmed by the use of a different column (didecyl phthalate on Celite) which produced a different series of relative retention times and also a different order of elution from the column as follows: acetone (0·44), t-butyl alcohol (0·56), t-butyl bromide (0·82), carbon tetrachloride (1·00), t-butyl hypobromite (1·10), the unknown component (X) (1·31), and bromotrichloromethane (2·52). This assignment was confirmed by comparison with a synthetic mixture. The relative retention times were unaltered by variation of column temperature, etc. The composition (%) of the fraction is given in the Table. Analyses of fraction (*b*), under all of the conditions used above, revealed the presence of the same components, with the exception of carbon tetrachloride which was therefore added to provide a " marker " for the purpose of calculation of relative retention times. Analysis of fraction (*c*), which was carried out at a column temperature of 154° with a 2-m. " C " column (didecyl phthalate on Celite), indicated the presence of bromotrichloromethane (1·00), a new unidentified component (Y) (1·93), and hexachloroethane (4·06). This was confirmed by comparison with a synthetic mixture. The quantitative results together with those of a synthetic mixture are given in the Table.

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[22] Augood, Hey, and Williams, *J.*, 1952, 2094.

Quantitative analysis (% by wt.) on initiation–termination mixtures.

Component	Fraction (*a*)	Fraction (*b*)	Fraction (*c*)	Synthetic mixture Calc.	Synthetic mixture Found
Me_2CO	0·02	0·02	—	—	—
$Me_3C{\cdot}OH$	0·05	—	—	—	—
$Me_3C{\cdot}OBr$	6·30	5·10	—	2·8	2·8
Me_3CBr	0·86	0·62	—	1·0	1·0
CCl_4	0·38	—	—	3·3	3·4
$BrCCl_3$	92·3	94·2	99·2	92·9	92·8
Unknown X *	0·08	0·06	—	—	—
Unknown Y *	—	—	0·03	—	—
C_2Cl_6	—	—	0·75	—	—

* Weights obtained by difference.

A control experiment was carried out in which t-butyl hypobromite (46·3% by wt.) in carbon tetrachloride (53·7%) was fractionated, under the above conditions. Analysis of the fractions by gas–liquid chromatography indicated the partial decomposition of the hypobromite to give acetone, most of which was lost under the conditions of distillation. The new percentage composition of the mixture was found to be t-butyl hypobromite (34·0), carbon tetrachloride (64·2), and acetone (1·8). This allowed a correction to be made for loss of t-butyl hypobromite during distillation. A control experiment kindly performed by Mr. P. G. Hibbert confirmed that t-butyl hypobromite, but not t-butyl bromide, is formed during the decomposition of di-t-butyl peroxide in bromotrichloromethane in the absence of *trans*-stilbene.

Attempted Preparation of 1-*Bromo*-1,2-*diphenyl*-2-*t*-*butoxyethane*.—Bromine (4·5 g.) in t-butyl alcohol (50 ml.) was added to *trans*-stilbene (5 g.) in t-butyl alcohol (200 ml.) at 40—50° during 2 hr. The mixture was boiled and filtered whilst hot to leave 1,2-dibromo-1,2-diphenylethane (6·072 g.), m. p. 235—236°. t-Butyl alcohol (100 ml.) was removed by distillation and the crystals of 1,2-dibromo-1,2-diphenylethane (0·168 g.) which separated on cooling were collected. The filtrate, on evaporation to dryness followed by recrystallisation of the residue from methanol, gave deoxybenzoin (0·3904 g., 7%), m. p. and mixed m. p. 55—56° (correct infrared spectrum).

Thermal Stability of 1-*Bromo*-2-*methoxy*-1,2-*diphenylethane*.—(i) The bromide (1·5 g.), m. p. 116—117° (from methanol), prepared by Jackson's method [23] (lit., m. p. 115—116°) was kept at 200° for 3 hr. After addition of ethanol (1 ml.), filtration gave 1,2-dibromo-1,2-diphenylethane (0·32 g.), m. p. and mixed m. p. 234—236°. Evaporation of the filtrate left a residue which, on fractional crystallisation from methanol, gave 1,2-dibromo-1,2-diphenylethane (0·03 g.), m. p. and mixed m. p. 231—234°, *trans*-stilbene (0·38 g., 41%), m. p. and mixed m. p. 121—123°, and deoxybenzoin (0·20 g., 20%), m. p. and mixed m. p. 55—56°.

(ii) Partial decomposition of the starting material occurred at 130—135°/45 mm. to the same products.

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[23] Jackson, *J. Amer. Chem. Soc.*, 1926, **48**, 2166.