

**965.** *The Activation of Carbon–Carbon Triple Bonds by Cationic Catalysts. Part I. The Interaction of Trichloroacetic Acid with Phenylacetylene in Benzene Solution.*

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Interaction of phenylacetylene and trichloroacetic acid in benzene has been studied. One molecule of the acid adds to the triple bond to form 1-phenylvinyl trichloroacetate. This reaction is of the first order in phenylacetylene and of the second in trichloroacetic acid. About 3% of polymer possessing a sequence of conjugated double bonds is also formed. A reaction scheme is proposed.

EARLIER work<sup>1</sup> has been concerned with the activation of carbon–carbon double bonds by cationic catalysts. In this Paper we extend our work to a triple-bond system.

#### EXPERIMENTAL

*Materials.*—The fraction of phenylacetylene (British Drug Houses) with b. p. 49–50°/15 mm. was used.<sup>2</sup> This was further distilled under a vacuum, stored in glass ampoules at 5° in the dark, and redistilled under a vacuum immediately before use.

Trichloroacetic acid and benzene were purified as described earlier.<sup>3</sup>

*Procedure.*—Reaction solutions were made up and introduced into dilatometers by the high-vacuum technique used to follow the reaction of trichloroacetic acid with 1,1-diphenylethylene.<sup>3</sup>

#### RESULTS

*Reaction Products.—Separation and identification.* The volume of the phenylacetylene–trichloroacetic acid–benzene system decreased gradually, the initially colourless solution becoming orange-brown. The solution was analysed by transferring it to a separatory funnel (the orange-brown colour persisting on exposure to air), and extracting it many times with water. Aliquot portions of these extracts were titrated against sodium hydroxide (phenolphthalein). The organic layer was separated into two fractions: (a) volatile fraction which contained benzene, phenylacetylene, and ~2% of acetophenone; and (b) a non-volatile fraction which was distilled under a vacuum; the pale yellow distillate, on repeated fractionation, gave a colourless liquid, b. p. 76–78°/10<sup>-2</sup> mm. (product A) which constituted not less than 95% of the total yield of crude product.

<sup>1</sup> Evans, James, and Owen, *J.*, 1961, 3532 and earlier Papers.

<sup>2</sup> Manchot and Hass, *Annalen*, 1913, 399, 150.

<sup>3</sup> Evans, Jones, and Thomas, *J.*, 1955, 1824.

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An orange-brown viscous gum (product B) remained, but attempts to precipitate polymeric material in a variety of non-solvents were unsuccessful. When the last traces of product A were removed by distillation under a vacuum, a very small amount of product B remained as a red-brown powder.

*Product A.*—(a) *Infrared spectrum.* This showed the presence of  $R_1R_2C=CH_2$ ,  $C_6H_5C=C$ ,  $-C(\cdot O)\cdot O-$ , and  $C-Cl$  groups, which are consistent with the structure  $CH_2\cdot CPh\cdot CO\cdot CCl_3$ .

(b) *Ultraviolet spectrum.* The salient features were (i) a strong absorption maximum at  $242.3\text{ m}\mu$  ( $\epsilon$  11,700), characteristic of conjugation between a phenyl group and an olefinic double bond, and (ii) shoulders between  $275$  and  $286\text{ m}\mu$  characteristic of a substituted benzene ring ( $\epsilon$  800 at  $274.8$ ;  $680$  at  $277.8$ ;  $450$  at  $285.7\text{ m}\mu$ ).

(c) *Molecular weight.* The molecular weight, determined cryoscopically in benzene solution, was  $262 \pm 5$ . (Calc. for  $C_{10}H_7Cl_3O_2$ :  $265.5$ ).

(d) *Elemental analysis.* Found: C,  $46.1$ ; H,  $2.7$ ; Cl,  $39.5$ . Calc. for  $C_{10}H_7Cl_3O_2$ : C,  $45.3$ ; H,  $2.7$ ; Cl,  $40.0\%$ .

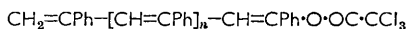
(e) *Hydrolysis.* Colourless product A was refluxed with sodium hydroxide solution. An  $80\%$  yield of acetophenone (identified by its semicarbazone and 2,4-dinitrophenylhydrazone derivatives) was obtained; the bulk of the remaining  $20\%$  was polymeric material. This shows that the most probable structure of product A is  $CH_2\cdot CPh\cdot CO\cdot CCl_3$  and not  $PhCH\cdot CH\cdot OCO\cdot CCl_3$ .

*Product B.* The orange-brown solid (B) was about  $3\%$  of the total product. Since it was obtained by distilling from the reaction products the last traces of 1-phenylvinyl trichloroacetate (A) at  $78^\circ/10^{-2}\text{ mm}$ . it had been subjected to degradative conditions.

(a) *Elemental analysis.* A sample obtained under strong degradative conditions gave C,  $84.9$ ; H,  $4.8$ ; Cl,  $1.7\%$ . A sample obtained under mild degradative conditions gave C,  $78.4$ ; H,  $4.11$ ; Cl,  $7.4\%$ .

(b) *Molecular weight.* Determined cryoscopically in benzene this was  $605 \pm 50$ , which corresponds to a polymer containing 5–6 monomer units.

(c) *Infrared spectra.* These were in accord with the structure:



(d) *Ultraviolet and visible spectra.* These were in agreement with the above structure of product B.

*Kinetic Measurements.—Orders of reaction.* The order of reaction in phenylacetylene was found to be  $1.0 \pm 0.1$  from the dependence of the initial rate of volume contraction ( $R_i$ ) on the initial phenylacetylene concentration at constant acid concentration and reaction temperature (see Table 1). In a similar manner, the order of reaction in trichloroacetic acid was found to be  $2.0 \pm 0.2$  (see Table 2).

TABLE 1.

Reaction order in phenylacetylene at $30^\circ$ . $[(Cl_3C\cdot CO_2H)_2]_i^* = 0.307\text{ mole l.}^{-1}$ .				
$[C_6H_5C\cdot CH]_i$ (mole $l.^{-1}$ ) .....	0.455	0.637	0.91	1.365
$10^2 R_i$ (ml. $l.^{-1}\text{ hr.}^{-1}$ ) .....	3.02	4.33	6.33	8.74
$10^2 R_i/[C_6H_5C\cdot CH]_i$ (ml. $l.^{-1}\text{ hr.}^{-1}$ ) .....	6.64	6.79	6.95	6.40

\* The trichloroacetic acid has been considered as dimeric in benzene.<sup>4</sup>

TABLE 2.

Reaction order in trichloroacetic acid at $30^\circ$ . $[C_6H_5C\cdot CH]_i = 0.91\text{ mole l.}^{-1}$ .						
$[Cl_3C\cdot CO_2H]_i^*$ (mole $l.^{-1}$ ) .....	0.071	0.142	0.178	0.307	0.355	0.425
$10^2 R_i$ (ml. $l.^{-1}\text{ hr.}^{-1}$ ) .....	0.31	1.00	1.72	6.34	8.06	11.14
$10 R_i/[(Cl_3C\cdot CO_2H)_2]_i^2$ (ml. $l.^{-1}\text{ hr.}^{-1}\text{ mole}^{-2}$ ) .....	6.08	4.97	5.42	6.73	6.40	6.17

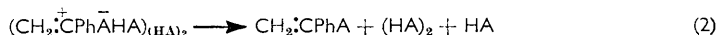
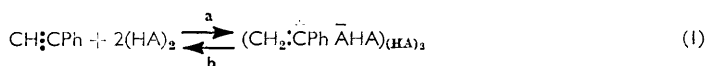
\* The trichloroacetic acid has been considered as dimeric in benzene.<sup>4</sup>

*Temperature-dependence.* Plotting  $\log_{10} R_i$  against  $1/T$  at constant phenylacetylene ( $0.91M$ ) and trichloroacetic acid ( $0.204M$ ) concentrations gave a value of  $12.0 \pm 1.0$  kcal. per mole for the activation energy ( $R_i$  in  $10^{-2}\text{ ml. l.}^{-1}\text{ hr.}^{-1} = 4.07$  at  $30$ ,  $6.23$  at  $40$ , and  $16.4$  at  $55^\circ$ ).

## DISCUSSION

*Mechanism of Reaction.*—The mechanism must satisfy the following: (a) The reaction is of the first order in phenylacetylene and of the second order in trichloroacetic acid. (b) The main reaction is the addition of one molecule of acid to phenylacetylene to form 1-phenylvinyl trichloroacetate,  $\text{CH}_2\text{:CPhO}_2\text{C}\cdot\text{CCl}_3$ , which forms never less than 95% of the total product. (c) A small amount of acetophenone is obtained. (d) A small amount of a polymer of low molecular weight possessing a sequence of conjugated double bonds is also obtained. (e) Trichloroacetic acid is dimeric in benzene.<sup>4</sup>

We postulate the mechanism:



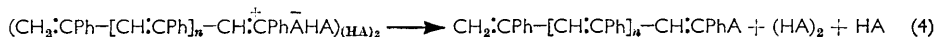
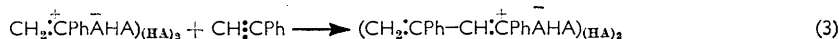
where  $(\text{HA})_2$  represents a molecule of dimeric acid.

In this scheme a molecule of  $(\text{HA})_2$  interacts with the triple bond to add a proton, and the ion pair so formed is solvated by a further molecule of  $(\text{HA})_2$ . Trichloroacetic acid also acts in this dual role when it catalyses the dimerisation of 1,1-diphenylethylene in benzene.<sup>3</sup> The order of reaction will be unity in phenylacetylene and two in acid if reaction (1a) is rate-determining, or if equilibrium (1) lies well to the left and reaction (2) is rate-determining. The activation energy (12 kcal. mole<sup>-1</sup>) will be equal to  $\Delta H_{1a}$  or to  $\Delta H_{1a}^\circ + \Delta H_{2a}^\ddagger$  depending on whether reaction (1a) or (2) is rate-determining.

It may be that the solvated ion pair of equation (1) is formed by the reaction of one molecule of acid with a molecule of acetylene which is already complexed with an acid molecule. If the equilibrium concentration of these complexed acetylene molecules were low and rapidly established, this mechanism would also give a reaction order 2 in acid.

The formation of acetophenone may take place by the addition of a further molecule of acid either to the ion pair or to the ester.

The polymeric material possessing a sequence of conjugated double bonds will probably be formed as follows:



1-Phenylvinyl trichloroacetate and trichloroacetic acid reacted in benzene, giving acetophenone and a small amount of polymer (a trace of the acetylene could be detected during the first 15% of this reaction). This formation of acetophenone from ester and acid was much slower than that of the ester from the acetylene and acid.

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<sup>4</sup> Bell and Arnold, *J.*, 1935, 1432.