344. *The Relative Stabilising Influences of Substituents on Free Alkyl Radicals. Part I. The Addition of Bromotrichloromethane and Butanal to Unsaturated Acids, Esters, and Nitriles.*

By R. L. Huang.

The homolytic addition of bromotrichloromethane and butanal to unsymmetrical olefins CHR:CHR′ (ethyl crotonate, crotonic acid, ethyl hydrogen maleate, ethyl β-acetylacrylate, ethyl cinnamate, and *cis*- and *trans*-cinnamonitrile) has been studied. Since, steric factors being absent, addition proceeds *via* the radical (say CHXR·CHR′·) of the greater stability, identification of the adduct in each case affords a comparison of the stabilising effect of R and R′ on the alkyl radical. It is thus shown that the relative effects are : Ph > CO_2Et, CN; CO > CO_2Et > CO_2H > Me.

The properties of free alkyl radicals differ markedly according to the nature of substituent groups, exhibiting extreme activity in free methyl and ethyl, and relative stability in free benzyl and other radicals containing unsaturated groups. In general, substituent groups capable of resonance with the free radical centre confer stability, as in the free radicals derived from alkylbenzenes,[1] allylbenzene,[2] ketones,[3] etc. No attempt, however, has yet been made to compare the relative stabilising effects of such groups; this work concerns such a study.

It is now established that, where steric factors do not intervene, the course of a homolytic reaction depends on the relative stability of the intermediate free radical involved (for a review, see Huang [4]). In the addition, therefore, of a substance XY to an unsymmetrical olefin CHR:CHR′ by the usual chain mechanism involving, say, the addition of X· as the initiating step (reaction 1), the intermediate alkyl radical (I) or (II) would be formed according to whether R or R′, respectively, confers the greater stability on the intermediate radical. [Haszeldine's postulate [5] need not be considered here since both (I) and (II) contain the same number of hydrogen atoms at the radical centre.] Two products are therefore possible and, provided steric factors are absent or unimportant, identification of the adduct would reveal whether R or R′ is more effective as a stabilising substituent :

$$\text{X}\cdot + \text{CHR:CHR}' \longrightarrow \cdot\text{CHR·CHR}'\text{X (I) or CHXR·CHR}'\cdot \text{ (II)} \quad . \; . \; . \quad (1)$$

$$\text{(I)} + \text{XY} \longrightarrow \text{CHYR·CHR}'\text{X} + \text{X}\cdot \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

or

$$\text{(II)} + \text{XY} \longrightarrow \text{CHXR·CHR}'\text{Y} + \text{X}\cdot \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

This paper reports a study of some homolytic additions to crotonic acid and its ethyl ester, ethyl hydrogen maleate, ethyl β-acetylacrylate, ethyl cinnamate, and *cis*- and *trans*-cinnamonitrile.

In the above chain mechanism, no addition takes place if the initiating reaction (1) fails. On the other hand, if the propagation step (2) is slow, the intermediate radical (I) or (II) might (*a*) react with the olefin to form telomers, or (*b*), at higher concentration, undergo chain termination by disproportionation or dimerisation. Such side reactions might obscure the main course of the reaction. Since a yield of over 50% is essential for a reliable evaluation of the stabilising influence of the competing groups, the choice of the reagent XY is critical. The substances which are known to add to olefins and have been well investigated are the polyhalogenated methanes, aliphatic aldehydes and α-bromo-esters (for a review, see Cadogan and Hey [6]). Of these, bromotrichloromethane (the initiating radical being $Cl_3C\cdot$) was chosen as the only readily available reagent for such reactions for

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[1] Huang and Lee, *J.*, 1954, 2570.

[2] Kharasch, Schwartz, and Nudenberg, *J. Org. Chem.*, 1953, **18**, 337.

[3] Kharasch, McBay, and Urry, *J. Amer. Chem. Soc.*, 1948, **70**, 1269.

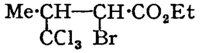
[4] Huang, *J.*, 1954, 3084.

[5] Haszeldine, *J.*, 1953, 3565.

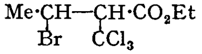
[6] Cadogan and Hey, *Quart. Rev.*, 1954, **8**, 308; cf. Kharasch, Skell, and Fisher, *J. Amer. Chem. Soc.*, 1948, **70**, 1055.

nearly all olefins, even styrene.[7] Aliphatic aldehydes, especially butanal, add well to certain olefins, but in some cases lead to formation of telomers, *e.g.*, with ethyl fumarate,[8] and in others do not add at all, notably to substances in which the olefinic double bond is conjugated with a benzene ring, as in benzylideneacetone.[9] Where applicable, however, the use of butanal is convenient, in that the structures of the resulting adducts can often be easily elucidated. Both these reagents have therefore been employed, with benzoyl peroxide as the catalyst.

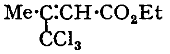
Addition of bromotrichloromethane to ethyl crotonate gave the ester (III) in 84% yield. This was converted smoothly, by potassium acetate in hot acetic acid or by potassium hydroxide in cold ethanol, into the butenoate (IV), which in turn, with concentrated sulphuric acid, gave mesaconic acid. Thus the adduct has structure (III) and not the alternative (III*a*). Since the intermediate radical (V) was clearly involved, ethoxycarbonyl is more stabilising than methyl.


$\mathrm{Me{\cdot}\underset{CCl_3}{C}H{-}\underset{Br}{C}H{\cdot}CO_2Et}$

(III)

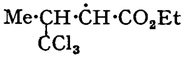

$\mathrm{Me{\cdot}\underset{Br}{C}H{-}\underset{CCl_3}{C}H{\cdot}CO_2Et}$

(III*a*)


$\mathrm{Me{\cdot}\underset{CCl_3}{C}{:}CH{\cdot}CO_2Et}$

(IV)

(V)

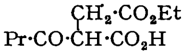

$\mathrm{Me{\cdot}\underset{CCl_3}{C}H{\cdot}\dot{C}H{\cdot}CO_2Et}$

$\mathrm{Pr{\cdot}CO{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2Et}$ (VI)

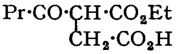
Addition of butanal to the same ester afforded a 77% yield of the γ-keto-ester (VI) which on hydrolysis furnished the corresponding keto-acid. The identity of the adduct is hence beyond doubt, since the alternative mode of addition would have led to a β-keto-ester, which would have been decarboxylated on hydrolysis. This result confirms the previous finding.

Addition of butanal to crotonic acid led to an excellent yield (83%) of the same γ-keto-acid. The carboxyl group is therefore a more effective stabilising group than methyl. It is of interest to note the isolation in the neutral fraction of the product of small quantities of butyroin, formed probably by the action of the butyryl radical on butanal. The formation of acetoin by ultraviolet irradiation of acetaldehyde and of pyruvic acid[10] probably proceeds by a similar mechanism.

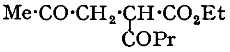
The products of addition of butanal to ethyl hydrogen maleate were separated into a neutral and an acid fraction. The former and main fraction consisted chiefly of ethyl 4-oxoheptanoate (49% overall yield) which in all probability was formed by decarboxylation of the β-keto-acid (VII), derived in turn *via* an initial radical addition to the carbon atom adjacent to the carboxyl group in ethyl hydrogen maleate. (It is not known whether decarboxylation occurred with the intermediate radical or the final addition product.) The acidic fraction was a mixture from which were isolated, after alkaline hydrolysis, small quantities of 4-oxoheptanoic acid. This could be obtained by the hydrolysis and partial decarboxylation of the alternative adduct (VIII). Since the adduct (VII) appears to be the main product it is reasonable to conclude that the ester group is more stabilising than the acid group.


$\mathrm{Pr{\cdot}CO{\cdot}\overset{CH_2{\cdot}CO_2Et}{C}H{\cdot}CO_2H}$

(VII)


$\mathrm{Pr{\cdot}CO{\cdot}\underset{CH_2{\cdot}CO_2H}{C}H{\cdot}CO_2Et}$

(VIII)


$\mathrm{Me{\cdot}CO{\cdot}CH_2{\cdot}\underset{COPr}{C}H{\cdot}CO_2Et}$

(IX)

$\mathrm{Me{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COPr}$

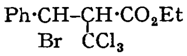
(X)

Ethyl β-acetylacrylate and butanal gave an adduct (56% yield) which exhibited the usual properties of a keto-enol system and on hydrolysis with potassium carbonate suffered decarboxylation also, to give the diketone (X). The adduct must therefore be the β-keto-ester (IX), the formation of which indicates the greater stabilising influence of the ketonic group.

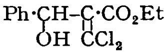
In ethyl cinnamate the steric factors might seem capable of assuming significant proportions. However, Fisher–Taylor–Hirschfelder models of the two possible adducts

[7] Kharasch, Simon, and Nudenberg, *J. Org. Chem.*, 1953, **18**, 328.
[8] Patrick, *ibid.*, 1952, **17**, 1009.
[9] *Idem, ibid.*, p. 1269.
[10] Dirscherl, *Z. physiol. Chem.*, 1938, **219**, 177.

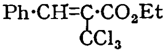
with bromotrichloromethane showed both molecules to be strainless and, since the addition does not involve a transition state with higher compression than the end-product, the steric picture can be discounted. Addition of bromotrichloromethane to ethyl cinnamate furnished a crystalline adduct (72% yield) which was converted by boiling aqueous-alcoholic potassium hydroxide into benzylidenemalonic acid. The structure of the adduct must therefore be (XI). Treatment with potasium hydroxide in cold ethanol, however, gave a partially dechlorinated neutral substance, probably (XII), formed presumably by partial hydrolysis during isolation of the allylic chloride (XIII). Hydrolysis of the product (XII) with acetic acid containing perchloric acid [7] also furnished benzylidenemalonic acid. This contrast in behaviour of (XIII) with the allyl trichloride (IV) may be attributed to the stabilising effect of the benzene ring on the intermediate carbonium ion (XIV), by which the hydrolysis proceeds.


$Ph\cdot\underset{Br}{CH}-\underset{CCl_3}{CH}\cdot CO_2Et$

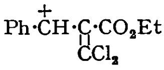
(XI)


$Ph\cdot\underset{OH}{CH}-\underset{\overset{\|}{CCl_2}}{C}\cdot CO_2Et$

(XII)


$Ph\cdot CH=\underset{CCl_3}{C}\cdot CO_2Et$

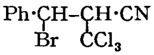
(XIII)


$Ph\cdot\overset{+}{C}H\cdot\underset{\overset{\|}{CCl_2}}{C}\cdot CO_2Et$

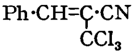
(XIV)

In view of Patrick's finding [9] that butanal does not add to benzylideneacetone, its addition to ethyl cinnamate was not carried out. An attempt to add ethyl bromoacetate, however, proved unsuccessful.

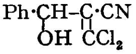
Addition of bromotrichloromethane to *cis*-cinnamonitrile gave, again in satisfactory yield, an adduct shown by degradation to be (XV). Isolation by crystallisation or distillation not proving feasible, the adduct was dehydrobrominated with potassium acetate in acetic acid, and was thereby obtained, not as the allyl trichloride (XVI), but as the partially hydrolysed (XVII) in a 56% overall yield calculated on the nitrile consumed. Hydrolysis of this with acetic acid and perchloric acid gave α-cyano-β-phenylacrylic acid, proving the structure.


$Ph\cdot\underset{Br}{CH}-\underset{CCl_3}{CH}\cdot CN$

(XV)


$Ph\cdot CH=\underset{CCl_3}{C}\cdot CN$

(XVI)


$Ph\cdot\underset{OH}{CH}-\underset{\overset{\|}{CCl_2}}{C}\cdot CN$

(XVII)

The same product (XVII) was obtained from *trans*-cinnamonitrile. However, the yield was considerably lower (33%), while the weight ratio between undistillable material and the adduct formed (approx. 1 : 1) was much increased (for the *cis*-nitrile the ratio was 1 : 2·2). Inasmuch as the same intermediate free radical is involved with both isomers, the high proportion of polymer in one case must be attributed, not to dimerisation of this intermediate radical, but to the formation of telomers as a result of different degrees of susceptibility of the isomeric nitriles towards attack by the same radical. This result is in contrast with those for ethyl crotonate and cinnamate, both of which are also *trans*, but parallels the addition of butanal to ethyl maleate and fumarate.[8]

Again in contrast with ethyl crotonate and cinnamate, more than 50% of either cinnamonitrile did not enter reaction, even though higher molar ratios of bromotrichloromethane and of the catalyst were employed for a longer reaction time. In view of the absence of hexachloroethane in the products, this indicates a short chain length rather than an inefficient initiating reaction.

The relative stabilising influence of the substituents so far studied are thus: $Ph > CO_2Et, CN$; $CO > CO_2Et > CO_2H > Me$.

EXPERIMENTAL

Addition of Bromotrichloromethane to Ethyl Crotonate.—A mixture of ethyl crotonate (20 g., 0·17 mole) and bromotrichloromethane (140 g., 0·70 mole) was heated at 80° under nitrogen while benzoyl peroxide (3·6 g., 0·015 mole) was added in 4 portions during 6 hr., the mixture being then further heated for 2 hr. On cooling, ether was added, and the solution extracted 4 times with 10% aqueous sodium hydrogen carbonate, to remove benzoic acid. After drying, the ether was removed, and the unchanged bromotrichloromethane (*ca.* 90 g.) recovered by distillation under a partial vacuum. Distillation of the residue then gave *ethyl 2-bromo-3-trichloromethylbutanoate*, b. p. 88—92°/1 mm. (46 g., 84%), and a yellow residue (7 g.). Redistillation of the main product gave a colourless liquid, b. p. 92—93°/1 mm., n_D^{22} 1·5007 (Found: C, 27·3; H, 3·5; Cl, 34·5. $C_7H_{10}O_2BrCl_3$ requires C, 26·9; H, 3·2; Cl, 34·1%).

Dehydrobromination.—(*a*) The above adduct (6·0 g., 0·02 mole) in cold absolute ethanol (5 c.c.) was added to a solution of potassium hydroxide (1·15 g., 0·02 mole) in the same solvent (15 c.c.). A white precipitate separated almost immediately and the mixture warmed slightly. After 2·5 hr. at room temperature (28°) a few drops of acetic acid were added, the solid (potassium bromide) was filtered off, and the filtrate concentrated to *ca.* 3 c.c. Aqueous sodium carbonate (10%) was added and the product extracted into ether, washed with water, dried, and concentrated. Distillation then gave *ethyl* 3-*trichloromethylbut*-2-*enoate*, b. p. 66—68°/1 mm., n_D^{22} 1·4912 (3·1 g., 66%) (Found: C, 36·7; H, 4·1; Br, 0. $C_7H_9O_2Cl_3$ requires C, 36·3; H, 3·9%).

(*b*) The above adduct (10·4 g.) was heated with potassium acetate (10 g.) and acetic acid (50 c.c.) on the steam-bath for 6 hr. The mixture was poured into water and neutralised with aqueous sodium carbonate, and the product isolated by extraction and distillation, giving the same butenoate as above (5·6 g., 73%).

Hydrolysis to mesaconic acid. The butenoate (1·3 g.), dissolved in twice its volume of concentrated sulphuric acid, was kept at room temperature for 24 hr., after which the solution was heated at 80° for 2 hr. It was then poured on ice (15 g.) and extracted with benzene (2 × 15 c.c.) and then with ether (5 × 15 c.c.). The ethereal extract, after being dried, was concentrated, giving mesaconic acid which, crystallised from ethanol–benzene, had m. p. 202° (lit., 202—204°) (0·15 g., 20%) (Found: C, 46·2; H, 4·75. Calc. for $C_5H_6O_4$: C, 46·2; H, 4·65%). Lower yields were obtained when heating was omitted or extended to 4 hr.

Addition of Butanal to Ethyl Crotonate.—Ethyl crotonate (23 g., 0·20 mole) and butanal (86 g., 1·2 moles) were heated at 80° under reflux in an atmosphere of nitrogen while benzoyl peroxide (3·7 g., 0·016 mole) was added in 4 portions during 6 hr. After 3 more hours' heating the excess of butanal was distilled off on the steam-bath, the last traces being removed by co-distillation with benzene. The residue was diluted with ether and extracted repeatedly with aqueous sodium hydrogen carbonate. After drying, the ether was removed and the product distilled, giving *ethyl* 3-*methyl*-4-*oxoheptanoate*, b. p. 81—83°/2 mm., n_D^{22} 1·4271 (29 g., 77%) (Found: C, 64·2; H, 9·9. $C_{10}H_{18}O_3$ requires C, 64·5; H, 9·7%). The *semicarbazone*, needles from aqueous ethanol, had m. p. 96—97° (Found: N, 17·3. $C_{11}H_{21}O_3N_3$ requires N, 17·3%). The keto-ester was unaffected by a boiling 10% solution of potassium carbonate in 80% aqueous ethanol for 6 hr.

This ester (9·0 g.) was boiled with 5% aqueous sodium hydroxide (70 c.c.) for 3·5 hr. by which time the mixture had become homogeneous. It was cooled and extracted twice with ether, then acidified with dilute sulphuric acid, and the acid was taken up in ether, dried, and distilled, giving 3-*methyl*-4-*oxoheptanoic acid*, b. p. 126°/3 mm., n_D^{22} 1·4414 (6·2 g.) (Found: C, 61·1; H, 9·0. $C_8H_{14}O_3$ requires C, 60·7; H, 8·9%). The *semicarbazone*, recrystallised from 90% ethanol, had m. p. 176—178° (Found: N, 19·8. $C_9H_{17}O_3N_3$ requires N, 19·5%).

Addition of Butanal to Crotonic acid.—Benzoyl peroxide (1·9 g., 0·008 mole) was decomposed in a solution of crotonic acid (8·0 g., 0·09 mole) in butanal (40 g., 0·56 mole) at 80° in the usual way. After removal of unused butanal, ether was added, and the acidic product taken up in 20% aqueous sodium carbonate (4 × 40 c.c.) which was washed twice with ether, acidified with 5N-sulphuric acid, and extracted with ether (4 × 60 c.c.). This extract was washed with water, dried, and distilled, to give 3-methyl-4-oxoheptanoic acid, b. p. 90—92°/0·5 mm. (12·6 g.), contaminated probably with benzoic acid. A sample (1·01 g.) of the distillate gave a good yield (1·12 g.) of the semicarbazone, m. p. 175°, alone or mixed with that obtained in the previous experiment. By comparison with the yield of semicarbazone obtained from a pure sample of the keto-acid under identical conditions, the above distillate was estimated to contain *ca.* 94% of the keto-acid. The yield was therefore 83%.

The neutral fraction remaining in the ethereal solution after alkali-extraction was concentrated and distilled, giving a fraction, b. p. 71—80°/1 mm., n_D^{23} 1·4295 (1·9 g.), and a viscous residue (2 g.). The former was further distilled evaporatively, giving a colourless liquid, n_D^{23} 1·4269 (Found: C, 67·0; H, 11·2. Calc. for butyroin, $C_8H_{16}O_2$: C, 66·6; H, 11·2%). Corson Benson, and Goodwin [11] report, for butyroin, b. p. 80—82°/10 mm., n_D^{26} 1·4242. When warmed with Brady's reagent it readily formed *octane*-3 : 4-*dione bis*-2 : 4-*dinitrophenylhydrazone* which crystallised from ethanol in needles, m. p. 109—110° (Found: C, 47·7; H, 4·8; N, 21·9. $C_{20}H_{22}O_8N_8$ requires C, 47·8; H, 4·4; N, 22·3%).

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[11] Corson, Benson, and Goodwin, *J. Amer. Chem. Soc.*, 1930, **52**, 3988.

Addition of Butanal to Ethyl Hydrogen Maleate.—Ethyl hydrogen maleate, prepared by Shields's method[12] in 8% yield, had b. p. 110°/1 mm., n_D^{22} 1·4590 (Found: C, 50·4; H, 5·9. Calc. for $C_6H_8O_4$: C, 50·0; H, 5·6%).

The product from ethyl hydrogen maleate (7·0 g., 0·05 mole), butanal (22 g., 0·3 mole), and benzoyl peroxide (2·0 g., 0·008 mole) was dissolved in ether, and separated by extraction with 10% aqueous sodium hydrogen carbonate (5 × 20 c.c.) into a neutral and an acidic fraction. The neutral fraction (7·4 g.) was distilled, giving mainly *ethyl* 4-*oxoheptanoate*, b. p. 50—54°/1 mm., n_D^{23} 1·4278 (4·0 g., 49%) (Found: C, 63·2; H, 9·55. $C_9H_{16}O_3$ requires C, 62·8; H, 9·4%), whose *semicarbazone*, needles from aqueous ethanol, had m. p. 107—109° (Found: N, 18·4. $C_{10}H_{19}O_3N_3$ requires N, 18·3%). Hydrolysis by boiling 10% aqueous sodium hydroxide for 3 hr. gave a good yield of the keto-acid, m. p. 46—46·5° (lit., m. p. 47—48°), which formed a *semicarbazone*, m. p. 150—152° (from aqueous ethanol) (Found: N, 20·8. $C_8H_{15}O_3N_3$ requires N, 20·9%). The keto-acid and its methyl ester have been reported by Ladd.[13] The residue (2·8 g.) from the above distillation was further distilled, giving two small fractions of varying refractive indices, b. p. 110—120° (bath)/0·5 mm. (total 1·1 g.) (which gave very small quantities of solid derivatives with Brady's reagent and with semicarbazide), and an undistillable residue (1·3 g.), all of which were not further investigated.

The hydrogen carbonate extract was acidified with 5N-sulphuric acid and extracted with ether, dried, and concentrated to a viscous liquid. A solid (0·8 g.) which separated crystallised from light petroleum; it was benzoic acid (m. p. and mixed m. p.), more of which (0·9 g.) sublimed on subsequent heating of the liquid at 0·5 mm. The residual liquid (2·7 g.) was divided into portions A and B. A (1·7 g.) was distilled, giving a colourless liquid, b. p. 120—135° (bath)/0·5 mm. (0·48 g.), which did not exhibit ketonic properties. The portion B (1·0 g.) was dissolved in 10% aqueous potassium hydroxide (10 c.c.), kept for 20 hr. at room temperature, then heated at 100° for 1 hr. The solution was acidified with sulphuric acid, extracted with ether, dried, and evaporated to a viscous oil. This gave 4-ketoheptanoic acid semicarbazone (0·09 g.), m. p. 149—150°, alone or mixed with the specimen obtained previously. To estimate the approximate amount of the keto-acid present in the mixture, an authentic sample was treated with semicarbazide under comparable conditions and the yields were compared. It was thus estimated that a total of 0·27 g. of 4-oxoheptanoic acid would be obtained by hydrolysis of the whole acidic fraction, corresponding to 0·32 g. or 3·3% of 2-ethoxycarbonyl-4-oxoheptanoic acid.

Addition of Butanal to Ethyl β-*Acetylacrylate.*—The acrylate, prepared from ethyl lævulate by bromination at 0° in ether solution followed by dehydrobromination with potassium acetate in acetic acid at 100°, had b. p. 48—50°/1 mm., n_D^{23} 1·4460 (cf. Wolff[14]). After being heated at 70° for 12 hr. with butanal (43 g., 0·6 mole) and benzoyl peroxide (2·4 g., 0·01 mole), the acrylate (14 g. 0·1 mole) gave, on distillation, (i) unchanged acrylate (2·5 g.), (ii) *ethyl* 2 : 5-*dioxo-octane*-4-*carboxylate*, b. p. 89—92°/0·5 mm., n_D^{23} 1·4445 (9·2 g., 54%) (Found: C, 62·0; H, 8·4; O, 30·0. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·5; O, 29·9%), and (iii) a yellowish residue, which did not distil at 150° (bath)/0·5 mm. (6 g.). This adduct was soluble in 30% aqueous sodium hydroxide, gave a violet colour with ferric chloride, and decolorised bromine instantly in chloroform. (The starting material did not exhibit the first two properties, and decolorised bromine relatively slowly.) When treated with aqueous-alcoholic semicarbazide (with sodium acetate) at 80° or in the cold the adduct reacted with elimination of two mols. of water, to give in good yield a solid *derivative*, probably a pyrrole derivative (cf. reaction of acetonylacetone with oxalyl dihydrazide[15]) which crystallised from ethanol in needles, m. p. 238° (Found: C, 57·3; H, 7·7; N, 16·45. $C_{12}H_{19}O_3N_3$ requires C, 56·9; H, 7·6; N, 16·6%).

Hydrolysis and decarboxylation. The above product (3·5 g.) was heated under reflux with potassium carbonate (3·5 g.) in water (15 c.c.) and ethanol (10 c.c.) for 6 hr. The ethanol was removed under a partial vacuum, and the product extracted into ether, washed once with a little water, dried, and concentrated. Distillation gave *octane*-2 : 5-*dione*, a hygroscopic liquid, b. p. 60° (bath)/0·5 mm. or 105° (bath)/15 mm., n_D^{23} 1·4317 (1·4 g., 61%) (Found: C, 67·8, 67·4; H, 9·7, 10·3. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%). This reacted with semicarbazide, with elimination of two mols. of water, to form a solid *derivative*, m. p. 172°, which crystallised from ethanol in needles (Found: C, 59·5; H, 8·15; N, 23·0. $C_9H_{15}ON_3$ requires C, 59·6; H, 8·3; N, 23·2%).

Addition of Bromotrichloromethane to Ethyl Cinnamate.—Ethyl cinnamate (35 g., 0·2 mole),

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[12] Shields, *J.*, 1891, **59**, 736.

[13] Ladd and U. S. Rubber Co., U.S.P. 2,577,133/1951; B.P. 636,287/1950.

[14] Wolff, *Annalen*, 1891, **264**, 248.

[15] Bülow, *Ber.*, 1905, **38**, 3914.

bromotrichloromethane (160 g., 0·8 mole), and benzoyl peroxide (4 g., 0·016 mole) gave, after removal of benzoic acid, unchanged bromotrichloromethane, ethyl cinnamate (14 g.) (bath highest at 140°/0·2 mm.), and a yellow viscous liquid (40 g.) which on treatment with chilled methanol deposited *ethyl* β-*bromo*-β-*phenyl*-α-*trichloromethylpropionate*, m. p. 56—60° (23 g.), which crystallised from methanol in pale yellow prisms, m. p. 65·5° (Found: C, 38·9; H, 3·5; O, 8·6; Cl, 28·2. $C_{12}H_{12}O_2BrCl_3$ requires C, 38·5; H, 3·2; O, 8·5; Cl, 28·4%). The filtrate was concentrated to a pale yellow oil (16 g.), a portion of which (4 g.) on treatment with cold alcoholic potassium hydroxide as for the solid [see (*b*) below] gave the same product, b. p. 135° (bath)/1 mm., n_D^{22} 1·5330 (1·7 g.), showing that this oil contained approx. 60% by weight of the above solid. The total yield was therefore approx. 72%, calculated on the ester consumed.

When a six-mol. excess of the halogenated methane and 12 mole% of benzoyl peroxide were used very little ethyl cinnamate was recovered, but the yield of adduct was not appreciably increased.

Dehydrobromination and hydrolysis. (*a*) The above adduct (1·4 g.) in absolute ethanol (10 c.c.) was added to a solution of potassium hydroxide (2·8 g.) in the same solvent (30 c.c.). The mixture was kept at room temperature for 2 hr., then refluxed for 4 hr. Water was added, and the ethanol removed under a partial vacuum, this being repeated, and the residual aqueous solution (15 c.c.) was then washed with ether three times and acidified with 5N-sulphuric acid. The precipitated acid was taken up in much ether. Removal of the ether gave a solid, which after recrystallisation from benzene–*cyclo*hexane, melted with efflorescence at 185° (115 mg., 16% overall), raised to 196—199° on further crystallisation (Found: C, 62·0; H, 4·3. Calc. for $C_{10}H_8O_4$: C, 62·5; H, 4·2%). A sample (2 mg.) after being heated at 200° for 1 min., cooled, and recrystallised from aqueous ethanol gave cinnamic acid, m. p. and mixed m. p. 131—133°. Liebermann [16] reports benzylidenemalonic acid, m. p. 195—196°, decomposing to cinnamic acid when heated.

(*b*) The above adduct (3·7 g., 0·01 mole) in absolute ethanol was added to a solution of potassium hydroxide (0·62 g., 0·011 mole) in the same solvent (20 c.c.) with cooling. After 5 hr. at 28° a few drops of acetic acid were added, and most of the ethanol was removed on the steam-bath. Ether was added, and the solution was washed repeatedly with 5% sodium hydrogen carbonate solution, dried, and concentrated to an oil (2·9 g.). The hydrogen carbonate washings on acidification gave no appreciable quantities of acidic material. The oil on distillation gave *ethyl* α-*dichloromethylene*-β-*hydroxy*-β-*phenylpropionate*, b. p. 114°/0·5 mm., n_D^{22} 1·5332 (2 g.) (Found: C, 52·0; H, 4·6; Cl, 25·9; O, 16·9. $C_{12}H_{12}O_3Cl_2$ requires C, 52·5; H, 4·4; Cl, 25·8; O, 17·4%).

(*c*) The above adduct (1·2 g.) was heated with potassium acetate (0·8 g.) and acetic acid (12 c.c.) on the steam-bath for 7 hr. and the product isolated in the usual way, giving the same product (0·61 g.) as in (*b*).

Hydrolysis with perchloric acid. The product from (*b*) above (0·5 g.) was boiled gently with acetic acid (5 c.c.) and 60% perchloric acid (0·5 c.c.) for 4 hr. Most of the acetic acid was removed by distillation under a partial vacuum, water was added (*ca.* 10 c.c.), and distillation continued until about 1 c.c. of water remained. This was extracted with ether, and the acid taken up in sodium hydrogen carbonate, washed with ether, precipitated by acidification, and again taken up in much ether. Evaporation of the ether yielded benzylidenemalonic acid (27 mg.), m. p. and mixed m. p. 197—199°.

Addition of Bromotrichloromethane to cis- *and* trans-*Cinnamonitrile.*—*cis*- and *trans*-Cinnamonitrile were prepared by decarboxylation of α-cyano-β-phenylacrylic acid in pyridine.[17] Three fractional distillations gave *cis*-isomer, b. p. 88—89°/2 mm., n_D^{22} 1·5882, and *trans*-isomer, b. p. 97—98°/2 mm., n_D^{22} 1·5988. Kistiakowsky [18] reports *cis* n_D^{20} 1·5843, *trans* n_D^{20} 1·6031.

cis-Cinnamonitrile (14 g., 0·11 mole) and bromotrichloromethane (140 g., 0·7 mole) were heated at 70° while benzoyl peroxide (3·2 g., 0·013 mole) was added in six portions during 8 hr., the mixture being then heated for 4 hr. more. After removal of benzoic acid, distillation recovered unchanged bromotrichloromethane and cinnamonitrile (8·5 g.), leaving a residue (11 g.) which was used directly for the next operation. (In another experiment attempts to isolate the adduct by distillation and crystallisation were unsuccessful.)

The crude product from the above (6 g.) was heated with potassium acetate (3·5 g.) and acetic acid (30 c.c.) at 100° for 7 hr. The mixture was poured into water and neutralised with sodium hydrogen carbonate, then isolated in the usual manner. Distillation afforded fractions: (i)

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[16] Liebermann, *Ber.*, 1893, **26**, 1572.

[17] Ghosez, *Bull. Soc. chim. belges*, 1932, **41**, 477.

[18] Kistiakowsky, *J. Amer. Chem. Soc.*, 1936, **58**, 2428.

b. p. 92—98°/1 mm. (0·8 g.); (ii) b. p. 105—120°/1 mm. (2·9 g., 56% overall yield, calc. on nitrile consumed); and (iii) an undistillable residue (1·3 g.). Fraction (ii) was further distilled, giving *α-dichloromethylene-β-hydroxy-β-phenylpropionitrile,* b. p. 110° (bath)/0·2 mm., n_D^{23} 1·5549 (Found : Cl, 31·1. $C_{10}H_7ONCl_2$ requires Cl, 31·1%).

The above propionitrile (0·35 g.) was gently boiled with acetic acid (2·5 c.c.) and 60% perchloric acid (0·3 c.c.) for 2·5 hr., and the product worked up in the usual way, giving α-cyano-β-phenylacrylic acid (0·115 g., 45%) which, crystallised from ethanol–benzene, had m. p. and mixed m. p. 181°. Prolonged heating (5 hr.) or use of a higher concentration of perchloric acid resulted in diminished yields.

Hydrolysis by a 10% solution of potassium hydroxide in refluxing 50% aqueous ethanol for 5 hr. gave a viscous oil.

trans-Cinnamonitrile gave the same propionitrile (33% yield), the identity being established by the boiling range, refractive index, analysis (Found : Cl, 31·1%), and hydrolysis with acetic–perchloric acid to α-cyano-β-phenylacrylic acid in approximately the same yield. The weight ratio of polymeric material : adduct obtained was higher than with *cis*-cinnamonitrile, being 1·5 : 1·6 and 1·7 : 1·5 in two experiments in which the dehydrobrominating agents were, respectively, potassium acetate in acetic acid, and potassium acetate in 90% ethanol. Dehydrobromination by methylaniline at 100° for 3 hr. gave on distillation a small yield of a product which became green. This method was therefore not investigated further.

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