921. *Olefinic Acids. Part IX.* α-Bromo-β-*tert.*-butyl- and α-Bromo-ββ-diphenyl-acrylic Acids.*

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α-Bromo-β-*tert.*-butylacrylic acid (III), in which αβ ⟶ βγ isomerisation of the double bond is impossible, has been synthesised. When it is treated with alkoxides, or aqueous sodium hydroxide, nucleophilic substitution of the halogen atom does not occur, but elimination takes place to give β-*tert.*-butylpropiolic acid (IX). The latter shows very low additive reactivity, but with alkoxides or alkali slowly gives the β-alkoxy(or hydroxy)-β-*tert.*-butylacrylic acid, and thence pinacolone.

The synthesis of α-bromo-ββ-diphenylacrylic acid is described. This acid, in which neither isomerisation nor elimination is possible, is very stable towards alkali.

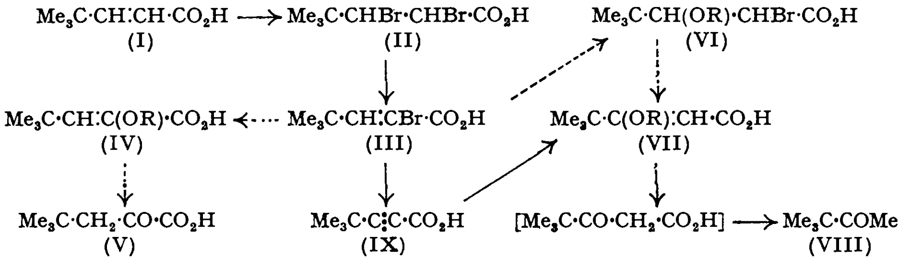
In the reactions of α-bromoacrylic acid with alkoxides (Owen and Somade, *J.*, 1947, 1030) no direct nucleophilic substitution of halogen could be detected, the main reaction being addition to the double bond, followed by elimination of hydrogen bromide, to give the β-alkoxy-acrylic acid :

$$CH_2{:}CBr{\cdot}CO_2H \longrightarrow RO{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2H \longrightarrow RO{\cdot}CH{:}CH{\cdot}CO_2H$$

The non-formation of any α-alkoxy-acrylic acid, in contrast to the results of similar reactions with α-bromocrotonic and α-bromo-ββ-dimethylacrylic acid, has been attributed (Owen and Sultanbawa, *J.*, 1949, 3089) to the impossibility of an initial rearrangement into an α-bromo-βγ-unsaturated acid, but it could be maintained that any direct substitution reaction would be rendered insignificant by the great susceptibility of the simple acrylic acid system, unsubstituted in the β-position, towards addition reactions. For this reason we have studied the preparation and properties of α-bromo-β-*tert.*-butylacrylic acid (2-bromo-4 : 4-dimethylpent-2-enoic acid) † (III), which also would be incapable of undergoing an αβ ⟶ βγ change, but would be expected to undergo addition much less readily.

4 : 4-Dimethylpent-2-enoic acid (I) (Foreman and McElvain, *J. Amer. Chem. Soc.*, 1940, **62**, 1438) with bromine in bright sunlight slowly gave 2 : 3-dibromo-4 : 4-dimethylpentanoic acid † (II); in the absence of sunlight the reaction was so slow as to be impracticable.

The proportions in which *cis*- and *trans*-α-bromo-αβ-unsaturated acids are formed by elimination of hydrogen bromide from an αβ-dibromo-acid, and the extent to which decarboxylation also occurs, sometimes depend on the reagent used (cf. Owen and Sultanbawa, *J.*, 1949, 3105; Part VIII *; and references there given). Dehydrobromination of (II) with aqueous sodium hydroxide, followed by precipitation of the product with hydrochloric acid, gave 2-bromo-4 : 4-dimethylpent-2-enoic acid (III), m. p. 68° (probably *trans*); dehydrobromination with pyridine caused also slight decarboxylation, but the main product was an acid which, although giving correct analyses for (III) and having similar light-absorption, had m. p. 55—62°, unchanged on further heating with pyridine containing pyridine hydrochloride, and on repeated sublimation, but raised to 68° on reprecipitation of the acid



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* Part VIII, preceding paper. † Geneva nomenclature, $CO_2H = 1$.

from alkaline solution with hydrochloric acid. It is probable that both reagents give a mixture containing a small proportion of *cis*-acid, but that the *trans*-isomer is obtained pure by precipitation from alkaline solution because of its lower solubility in water. Its structure was confirmed by ozonolysis to trimethylacetaldehyde.

Preliminary experiments showed that all the bromine was liberated as bromide ion on treatment of the unsaturated bromo-acid (III) for 15 hours at 80° with 2N-methanolic sodium methoxide or for 4 hours at 100° with 4N-aqueous sodium hydroxide. The solutions so obtained gave no ketonic reaction with 2 : 4-dinitrophenylhydrazine sulphate in acid solution. This proves that direct nucleophilic substitution did not occur, since this would have led to 2-keto-4 : 4-dimethylpentanoic acid (V), either directly (in the aqueous experiments) or by acid hydrolysis of the enol ether (IV). If, however, the heating with methoxide or alkali was greatly prolonged, or carried out with more concentrated solutions, or at a higher temperature, treatment with the reagent gave a small quantity of the 2 : 4-dinitrophenylhydrazone of pinacolone (VIII), the amount increasing with the time of heating. It was clear that this ketone was being formed by a reaction which was very much slower than the liberation of bromide ion ; this ruled out the possibility of the route *via* (VI) $\longrightarrow$ (VII).

It seemed likely that the initial reaction was one of elimination, to give 4 : 4-dimethylpent-2-ynoic acid (IX), followed by addition of methanol or water to form (VII), and this was confirmed in larger-scale experiments in which the acetylenic acid was isolated in good yield by treatment of (III) with aqueous sodium hydroxide, methanolic sodium methoxide, or potassium *tert.*-butoxide in *tert.*-butanol. It was characterised as the *p*-bromophenacyl ester and as the *S*-benzylthiuronium salt. When heated with aqueous sodium hydroxide it was slowly converted into pinacolone, the ketone being present in the alkaline reaction mixture, but with methanolic sodium methoxide pinacolone was only formed after acidification to hydrolyse the enol ether (VII; R = Me). Moureu and Delange (*Compt. rend.*, 1903, **136**, 552, 753) claimed that the acetylenic acid was not hydrated when treated with hot aqueous potassium hydroxide, but no doubt they were misled by the very slow reaction, which is in marked contrast to the behaviour of tetrolic acid (cf. Owen, *J.*, 1945, 385). The low additive reactivity of the olefinic acids (I) and (III) and the acetylenic acid (IX) can be attributed to the steric effect of the *tert.*-butyl group, which strongly hinders the attack by an anion or solvent molecule on the β-carbon atom ; the effect is similar to that which inhibits bimolecular substitution in the *neo*pentyl halides (Dostrovsky, Hughes, and Ingold, *J.*, 1946, 173). The *tert.*-butyl group, however, does not afford such protection to the hydrogen atom attached to the β-carbon atom in (III), so that an elimination (*E*2) reaction can occur comparatively readily. In this connection it is of interest that in the reaction of (III) with methanolic sodium methoxide there was gradual precipitation of sodium bromide; consequently the ionic strength of the solution was falling, and this should have had the same effect as a reduction in dielectric constant, which Cooper, Dhar, Ingold, Hughes, MacNulty, and Woolf (*J.*, 1948, 2043) have shown to increase slightly the rate of an *E*2 process of this type. The calculated bimolecular rate constants did in fact show a slight but definite increase as the reaction proceeded.

The complete absence of any direct substitution of the halogen atom in (III) is thus in accordance with our views on the mechanism of the reactions of various types of α-bromo-αβ-unsaturated acids with alkalis and alkoxides. The reported conversions, by alkali, of α-bromocinnamic acid (Glaser, *Annalen*, 1870, **154**, 146; Sudborough and Thompson, *J.*, 1903, **83**, 1155), α-bromo-*m*-methoxycinnamic acid (Jones and James, *J.*, 1935, 1600), and α-bromomaleic acid (Lossen and Menthal, *Annalen*, 1906, **348**, 308), into phenylpropiolic, *m*-methoxyphenylpropiolic, and acetylenedicarboxylic acid, respectively, appear to provide the only other known examples of the exclusive occurrence of elimination ; again it is evident that in none of these bromo-acids is there the possibility of αβ $\longrightarrow$ βγ change, so that direct replacement of bromine does not occur, and, furthermore, addition would be expected to occur only with difficulty.

A further consequence of the above argument is that the halogen atom would be expected to be very stable in a compound such as α-bromo-ββ-diphenylacrylic acid (X), in which neither prototropic change nor elimination can occur. ββ-Diphenylacrylic acid and bromine in bright sunlight gave αβ-dibromo-ββ-diphenylpropionic acid (XI), but attempts to dehydrobrominate this caused also decarboxylation to 2 : 2-diphenylvinyl bromide (XII). This difficulty was overcome by the use of the esters instead of the free acids. Addition of bromine to methyl ββ-diphenylacrylate, followed by dehydrobromination of the resulting dibromo-ester with sodium methoxide, proceeded smoothly, and alkaline hydrolysis then gave the required bromo-acid (X). The latter, in striking contrast to all the α-bromo-αβ-unsaturated acids previously studied, was practically unaffected by being heated for 2 days at 100° with a large excess of 3·7N-aqueous sodium hydroxide; similar treatment with 4N-methanolic sodium methoxide liberated only a very small proportion of the halogen as bromide ion.

$Ph_2C{:}CBr{\cdot}CO_2H$	$Ph_2CBr{\cdot}CHBr{\cdot}CO_2H$	$Ph_2C{:}CHBr$
(X)	(XI)	(XII)

EXPERIMENTAL

4 : 4-Dimethylpent-2-enoic acid (Foreman and McElvain, *loc. cit.*) was purified by sublimation at 50°/0·2 mm., the first fraction (m. p. 55—62°) being rejected. It was a highly crystalline solid, m. p. 61—62°, very soluble in all solvents except water, from which it separated as an oil. A portion recrystallised from pentane at −30° had m. p. 62—63° (Found : C, 65·6; H, 9·5%; equiv., 127. Calc. for $C_7H_{12}O_2$: C, 65·6; H, 9·4%; equiv., 128). Foreman and McElvain (*loc. cit.*) who record only the equivalent (128), give m. p. 62—63°.

The p-*bromophenacyl* ester separated from aqueous ethanol in plates, m. p. 98° (Found : C, 55·3; H, 5·3. $C_{15}H_{17}O_3Br$ requires C, 55·4; H, 5·3%).

2 : 3-*Dibromo*-4 : 4-*dimethylpentanoic Acid*.—Bromine (3·8 g.) and 4 : 4-dimethylpent-2-enoic acid (2·9 g.) in dry carbon tetrachloride (25 c.c.) were kept in bright sunlight for 6 hours. The solvent was removed at 30°/20 mm. and the residue was washed with ice-cold pentane (10 c.c.), and then recrystallised from pentane to give large prisms of 2 : 3-*dibromo*-4 : 4-*dimethylpentanoic acid* (3·35 g.), m. p. 93—94° (Found : Br, 55·9. $C_7H_{12}O_2Br_2$ requires Br, 55·5%). The mother-liquors gave a viscous oil.

Dehydrobromination of 2 : 3-*Dibromo*-4 : 4-*dimethylpentanoic Acid*.—(i) *With aqueous alkali.* 2·5N-Sodium hydroxide (20 c.c.) and the dibromo-acid (3·35 g.) at 55° gave a clear solution. After 24 hours at room temperature this was acidified with 6N-hydrochloric acid. The precipitated oil solidified on cooling and was washed with water (2 × 5 c.c.). The dried solid sublimed at 60°/0·2 mm. to a crystalline mass (2·04 g.) of 2-*bromo*-4 : 4-*dimethylpent*-2-*enoic acid* (probably *trans*), m. p. 68°, very soluble in all organic solvents (Found : C, 40·4; H, 5·4; Br, 38·7%; equiv., 207. $C_7H_{11}O_2Br$ requires C, 40·6; H, 5·4; Br, 38·6%; equiv., 207). Light absorption in ethanol : max. 2330 Å (ε 7200). Ether-extraction of the mother-liquors gave an acid, m. p. 55—63°, on sublimation at 50°/0·2 mm.

Treatment with aqueous sodium hydroxide of the evaporated mother-liquors obtained in the bromination of 4 : 4-dimethylpent-2-enoic acid gave the same acid (60%), m. p. 68°.

The unsaturated bromo-acid gave a p-*bromophenacyl* ester, needles (from aqueous ethanol), m. p. 92° (Found : C, 44·5; H, 4·0. $C_{15}H_{16}O_3Br_2$ requires C, 44·6; H, 4·0%).

(ii) *With pyridine.* 2 : 3-Dibromo-4 : 4-dimethylpentanoic acid (1·83 g.) was heated with dry pyridine (10 g.) at 65° in a stoppered flask for 2 hours, a precipitate of pyridine hydrobromide being gradually formed. Carbon dioxide was then detected, showing that some decarboxylation had occurred. Accordingly, after treatment of the mixture with excess of 2N-hydrochloric acid and extraction with ether, the pyridine-free ethereal solution was shaken with excess of saturated sodium hydrogen carbonate solution, and the ethereal and the aqueous layer were separated. The dried (Na_2SO_4) ethereal solution was evaporated to give a liquid residue (*ca.* 0·1 g.) which had an odour characteristic of a bromo-olefin, probably 1-bromo-3 : 3-dimethylbut-1-ene. The aqueous layer was acidified with 2N-hydrochloric acid and extracted with ether. Evaporation of the dried (Na_2SO_4) extracts and sublimation of the residue at 40°/0·2 mm. gave a solid (0·90 g.), m. p. 55—62°, mainly *trans*-2-bromo-4 : 4-dimethylpent-2-enoic acid with probably a small amount of the *cis*-isomer. The m. p. was unchanged after 2 further sublimations and after heating with pyridine containing a little pyridine hydrochloride for 2 hours at 100° (Found : Br, 38·7%; equiv., 207. Calc. for $C_7H_{11}O_2Br$: Br, 38·6%; equiv., 207). Light absorption in ethanol : max. 2330 Å (ε 6900).

The acid (0·42 g.) was dissolved in cold 3·7N-sodium hydroxide (6 c.c.) and kept for 24 hours at room temperature. On acidification with 2N-sulphuric acid a white crystalline solid was precipitated (0·3 g.) which after sublimation at 60°/0·2 mm. had m. p. and mixed m. p. 67° with *trans*-2-bromo-4 : 4-dimethylpent-2-enoic acid.

Ozonolysis of 2-*Bromo*-4 : 4-*dimethylpent*-2-*enoic Acid.*—The acid (0·34 g.) in dry carbon tetrachloride (10 c.c.) was ozonised at −10°; bromine was liberated. After removal of the solvent at 40°/25 mm. a colourless crystalline ozonide remained. This was decomposed at 100° for 30 minutes with zinc dust and 2N-acetic acid. Steam-distillation gave a distillate (5 c.c.), having a strong odour of trimethylacetaldehyde, which on treatment with 1% aqueous 2 : 4-dinitrophenylhydrazine sulphate gave the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 206° after recrystallisation from methanol.

Estimation of Pinacolone.—A standard solution of 2 : 4-dinitrophenylhydrazine sulphate was made by dilution of a solution of 2 : 4-dinitrophenylhydrazine (2·5 g.) in pure sulphuric acid (40 c.c.) with water (to 250 c.c.). A solution of pinacolone (12, 18, or 26 mg.) in water (15 c.c.) was added to 25 c.c. of the reagent, and after 1 week at room temperature the precipitated 2 : 4-dinitrophenylhydrazone was collected, washed with 2N-sulphuric acid (10 c.c.), then with water (5 c.c.), and dried at 56°/0·1 mm. The yields (22, 38, and 61 mg. respectively. Calc.: 35, 51, 74 mg.) showed that the loss due to solubility under these conditions is *ca.* 13 mg. This was taken into account in the corrected yields mentioned below.

Reaction of 2-*Bromo*-4 : 4-*dimethylpent*-2-*enoic Acid with Methanolic Sodium Methoxide.*—(i) Preliminary experiments were carried out to assess the reactivity of the bromine atom. Known weights of the acid (0·0005—0·001 g.-mol.) were heated with 4 equivalents of 2N-methanolic sodium methoxide in sealed glass tubes at 80° for various times (0—16 hours), the liberated bromide ion being estimated as described in the preceding paper.

Acid (g.)	2·0N-NaOMe–MeOH (c.c.)	Time (hours)	0·0960N-$AgNO_3$ (c.c.)	Reaction (%)	10^3k_2 (mol. l.$^{-1}$ min.$^{-1}$)
0·0970	0·94	1·5	1·08	22	1·9
0·1156	1·12	3	2·59	44	2·3
0·1026	0·99	6·25	4·08	79	3·3
0·1247	1·20	10·25	5·69	91	3·3
0·1090	1·05	15·5	5·39	98	3·8

(ii) The acid (0·0861 g.) and 2·5N-methanolic sodium methoxide (1·5 c.c.) were heated in a sealed tube at 100° for 16 hours. The contents were acidified with 2N-sulphuric acid, diluted to 15 c.c. with water, filtered, and added to the standard 2 : 4-dinitrophenylhydrazine reagent (25 c.c.). After 1 week the precipitate (m. p. 122°) was collected, washed, and dried by the standard procedure. The yield was 5 mg. (4%; corr. for loss, 14%).

(iii) As in (ii), but with only 8 hours' heating. No precipitation of 2 : 4-dinitrophenylhydrazone occurred.

(iv) 2-Bromo-4 : 4-dimethylpent-2-enoic acid (0·82 g.) was heated under reflux for 14 hours with 2·5N-methanolic sodium methoxide (10 c.c.). The first-formed granular suspension of the sodium salt of the bromo-acid dissolved on heating and a heavy precipitate of sodium bromide settled out as the reaction proceeded. The methanolic solution was diluted with water (100 c.c.), acidified with 2N-sulphuric acid, and immediately extracted with ether. Evaporation of the dried (Na_2SO_4) extracts gave a pale yellow liquid (0·44 g.) which solidified on distillation (b. p. 78°/0·7 mm.), giving hygroscopic needles, m. p. 39—45°. Redistillation (the first fraction, *ca.* 20 mg., being rejected) gave crystalline 4 : 4-dimethylpent-2-ynoic acid, m. p. 44—47° (Found: equiv., 131. Calc. for $C_7H_{10}O_2$: equiv., 126). Moureu and Delange (*Compt. rend.*, 1903, **132**, 988) give m. p. 47—48°, b. p. 110°/10 mm.

The acid gave a p-*bromophenacyl* ester, needles, m. p. 107° (from aqueous ethanol) (Found: C, 55·7; H, 4·8. $C_{15}H_{15}O_3Br$ requires C, 55·7; H, 4·7%), and a S-*benzylthiuronium* salt which crystallised from aqueous methanol with slight decomposition as needles, m. p. 177—178° (decomp.) (Found: C, 62·2; H, 7·0. $C_{15}H_{20}O_2N_2S$ requires C, 61·6; H, 6·9%).

Reaction of 2-*Bromo*-4 : 4-*dimethylpent*-2-*enoic Acid with Potassium* tert.-*Butoxide.*—The bromo-acid (0·48 g.) was boiled under reflux with potassium *tert.*-butoxide in *tert.*-butanol (from potassium, 0·52 g., and *tert.*-butanol, 10 c.c.) for 4 days. The reaction was heterogeneous, white salts being continuously present. After removal of the solvent under reduced pressure the residue was dissolved in water and extracted with light petroleum (b. p. 40—60°) to remove decarboxylation products. The aqueous layer was acidified with 2N-sulphuric acid, filtered from silica, and extracted with ether, to give 4 : 4-dimethylpent-2-ynoic acid (0·14 g.), m. p. 44—47°.

Reaction of 2-*Bromo*-4 : 4-*dimethylpent*-2-*enoic Acid with Aqueous Alkali.*—(i) A solution of the acid (0·500 g.) in 3·7N-sodium hydroxide (5 c.c.) was heated at 100°; at intervals, portions were withdrawn and weighed, and the bromide ion was estimated as previously described. The % reaction was 90 (1 hr.), 97 (2 hr.), 100 (4 hr.).

(ii) A solution of the acid (0·12 g.) in 3·7N-sodium hydroxide (1 c.c.) was heated at 100° for

8 hours. Treatment with standard 2 : 4-dinitrophenylhydrazine reagent, as described above in the reactions with sodium methoxide, gave pinacolone 2 : 4-dinitrophenylhydrazone (3 mg., 2%; corr. for loss, 10%), m. p. 125°.

(iii) As in (ii), but 16 hours' heating. The yield was 10 mg. (6%; corr. for loss, 14%).

(iv) The acid (0·8 g.) was heated in 3·7N-sodium hydroxide (8 c.c.) at 100° for 6 hours and then steam-distilled; treatment of the distillate with aqueous 2 : 4-dinitrophenylhydrazine sulphate gave a small precipitate (4 mg.) of the pinacolone derivative, m. p. and mixed m. p. 125—126°. The residual alkaline solution was acidified and extracted with ether, to give 4 : 4-dimethylpent-2-ynoic acid (0·43 g.) [*S*-benzylthiuronium salt, m. p. 177—178° (decomp.)].

Formation of Pinacolone from 4 : 4-*Dimethylpent*-2-*ynoic Acid.*—(i) The acetylenic acid (90 mg.) was heated with 2·5N-methanolic sodium methoxide (1 c.c.) at 100° for 16 hours. The tube was broken under a slight excess of 0·5N-sulphuric acid, and the filtered solution (9 c.c.) was added to the standard 2 : 4-dinitrophenylhydrazine sulphate solution (25 c.c.). After 2 days the derivative was isolated as previously described (35 mg., 18%; corr. for loss, 24%), m. p. 123—125°, not depressed on admixture with pinacolone 2 : 4-dinitrophenylhydrazone).

(ii) The acid (50 mg.), heated with 3·7N-aqueous sodium hydroxide (1 c.c.) in a sealed tube at 100° for 24 hours, gave pinacolone 2 : 4-dinitrophenylhydrazone (30 mg., 27%; corr. for loss, 39%), m. p. and mixed m. p. 123—125°.

ββ-*Diphenylacrylic Acid.*—Ethyl β-hydroxy-ββ-diphenylpropionate (Rupe and Busolt, *Ber.*, 1907, **40**, 4537) (50 g.) in 90% formic acid (150 c.c.) and water (10 c.c.) was boiled under reflux for 3 hours, and then concentrated under reduced pressure. The product was poured into an excess of aqueous potassium carbonate, and the insoluble oil was removed in ether. Acidification of the aqueous portion then precipitated the unsaturated acid, which was collected, washed with water, and dried (11·5 g.; m. p. 157—159°).

The oil recovered from the ethereal extract was boiled under reflux for 3 hours with potassium hydroxide (10 g.) in ethanol (100 c.c.) and water (50 c.c.). The ethanol was then distilled off, more water was added, and a small amount of insoluble red oil (which contained some benzophenone) was removed in chloroform. Acidification of the aqueous solution then gave a further 22 g. of the unsaturated acid, m. p. 155—158° (total, 33·5 g., 81%). Recrystallisation from methanol gave flattened needles, m. p. 159—160°. Rupe and Busolt (*loc. cit.*) give m. p. 162°. This method is similar to that of Rupe (*Annalen*, 1913, **395**, 141), who recorded no yield, except that the use of potassium carbonate and hydroxide is advantageous in that it avoids the formation of the sparingly soluble sodium salt of the unsaturated acid. An attempt to carry out the dehydration with anhydrous formic acid was unsuccessful, most of the hydroxy-ester being recovered.

Methyl ββ-diphenylacrylate, obtained by methanol–sulphuric acid, had b. p. 130—132°/0·01 mm., n_D^{23} 1·6040. Posner (*J. pr. Chem.*, 1910, **82**, 439) gives b. p. 194·6—194·8°/13 mm.

αβ-*Dibromo*-ββ-*diphenylpropionic Acid.*—Bromine (0·8 g.) in dry carbon tetrachloride (1·5 g.) was added to the unsaturated acid (1·1 g.) in the same solvent (10 c.c., heated to dissolve the acid and then quickly cooled). In bright sunlight the solution rapidly became paler, and after several hours large colourless prisms (1·2 g.) were deposited from the orange-coloured solution. These darkened slowly when left at room temperature, and rapidly when heated alone or in carbon tetrachloride, chloroform, or benzene, but crystallised satisfactorily from dry ether on cautious addition of light petroleum (b. p. 40—60°), and gave the *dibromo-acid*, m. p. 99° (decomp.) (Found: C, 46·8; H. 3·4; Br, 41·5. $C_{15}H_{12}O_2Br_2$ requires C, 46·9; H, 3·15; Br, 41·6%).

2 : 2-*Diphenylvinyl Bromide.*—To a solution of the dibromo-acid (0·8 g.) in dry ethanol (10 c.c.) at −10° a solution of sodium (0·12 g.) in dry ethanol (5 c.c.) was slowly added (10 mins.). After storage at 0° overnight, the solution was diluted with water, and the insoluble bromine-containing oil was isolated by ether, to give 2 : 2-diphenylvinyl bromide (0·45 g.), m. p. 40—41°, unchanged on recrystallisation from methanol. Hepp (*Ber.*, 1874, **7**, 1410) gives m. p. 50°; Lipp (*Ber.*, 1923, **56**, 570) gives m. p. 41—42°. Acidification of the alkaline solution, and extraction with ether, gave only a trace of an acidic oil.

When a small amount of the dibromo-acid was dissolved in 2N-sodium carbonate the solution rapidly became cloudy; extraction with ether gave 2 : 2-diphenylvinyl bromide, m. p. 40°.

α-*Bromo*-ββ-*diphenylacrylic Acid.*—When bromine (3 g.) and methyl ββ-diphenylacrylate (4·5 g.) in dry carbon tetrachloride (20 c.c.) were exposed to sunlight the colour became paler, and after an hour the orange-coloured solution was evaporated at 40°/15 mm., the last traces of carbon tetrachloride being removed by distillation of small quantities of dry methanol. The crude dibromo-ester was dissolved in dry methanol (20 c.c.), cooled to −5°, and treated with a solution of sodium (1·5 g.) in dry methanol (20 c.c.), with stirring and cooling, at such a rate that the temperature did not rise above 0° (5 mins.). The solution was set aside at room temperature for 16 hours and then boiled under reflux for ½ hour. Water (4 c.c.) was added, and the solution boiled for a further ½ hour. Methanol was then distilled off, water being gradually added so that the final volume was *ca.* 50 c.c. On being cooled, the solution deposited long needles of a sparingly soluble sodium salt; this was collected, suspended in water (30 c.c.), and strongly acidified with hydrochloric acid, to give a solid acid (*A*). Acidification of the filtrate from the sodium salt gave a solid acid (*B*). Recrystallisation of (*A*) from aqueous methanol gave fluffy needles (2·25 g.) of *α-bromo-ββ-diphenylacrylic acid,* m. p. 148—150°, raised by one further crystallisation to 150°; the solvent of crystallisation was not readily removed by drying (Found, in material dried at 56°/0·01 mm.: C, 57·9; H, 4·25; Br, 24·9. Dried at 100°/0·01 mm.: C, 59·3; H, 3·75; Br, 26·2. $C_{15}H_{11}O_2Br$ requires C, 59·4; H, 3·65; Br, 26·4%). Recrystallisation of (*B*) from aqueous methanol gave material, m. p. 125—135°, which was not further examined.

Stability of the Halogen in α-Bromo-ββ-diphenylacrylic Acid.—(i) The bromo-acid (0·1 g.) was heated in 3·7N-sodium hydroxide (0·5 c.c.) in a sealed tube at 100° for 2 days. The liberated bromide ion, estimated as previously described, required 0·10 c.c. of 0·101N-$AgNO_3$, equiv. to 3% reaction. (ii) The bromo-acid (0·2 g.) and 4N-methanolic sodium methoxide (2 c.c.) were heated for 2 days at 100°; the liberated bromide ion required 0·65 c.c. of 0·101N-$AgNO_3$, equiv. to 10% reaction.

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