## 255. *The Relative Stabilising Influences of Substituents on Free Alkyl Radicals. Part II.* The Addition of Aliphatic Aldehydes to ββ-Dimethylacrylic Acid and its Derivatives.*

By R. L. HUANG.

The addition of aliphatic aldehydes R•CHO (R = $Pr^n$ and/or $n$-$C_6H_{13}$) to ββ-dimethylacrylic acid, ethyl ester, and nitrile, catalysed by benzoyl peroxide, has been studied. In each case the ratio of the isomeric adducts $R{\cdot}CO{\cdot}CMe_2{\cdot}CH_2X$ and $Me_2CH{\cdot}CHX{\cdot}COR$ is ascertained and this provides a basis for comparing the stabilising influence of X in $CMe_2{:}CHX$ on the intermediate alkyl radicals. It is thus found that $CN \approx CO > CO_2Et \approx CO_2H$. Some applications of the scale of stabilising influence obtained so far, *viz.*, $Ph > CN \approx CO > CO_2Et \approx CO_2H > Me$, are discussed.

IN Part I the homolytic addition of butanal and bromotrichloromethane to unsymmetrical olefins $R{\cdot}CH{:}CH{\cdot}R'$ was studied, and the mode of addition in each case afforded an intramolecular comparison of the stabilising influences of the substituents R and R′ on the free alkyl radicals. The scale of relative stabilising effects was: $Ph > CN, CO_2Et$; $CO > CO_2Et > CO_2H > Me$. We now report an intermolecular approach to the same objective, involving the addition of aliphatic aldehydes to ββ-dimethylacrylic acid and its derivatives. The results obtained in general confirm and extend previous findings.

* Part I, *J.*, 1956, 1749.

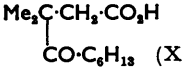
Addition of butanal to mesityl oxide (I; X = Ac) was shown by Patrick [1] to proceed with formation of the isomers (II) and (III) in a molar ratio of 10 : 1. In view of the possible presence of steric effects, and of the destabilising influence of a hydrogen atom [2] present in one of the possible intermediate radicals, *viz.*, (XVI*a* and *b*) (the initiating radical being $\mathrm{Pr\cdot\dot{C}O}$),[1, 3] this result cannot be interpreted as a ten-fold stabilising influence of the ketonic group compared with two methyl groups. However, addition of butanal to ethyl ββ-dimethylacrylate (I; X = $\mathrm{CO_2Et}$) has now been found to result in a 3 : 1 ratio of the isomers (IV) and (V), and, since the secondary effects just mentioned (steric and effect of a hydrogen atom) are identical in mesityl oxide and in the acrylate, the ratio of 10 : 1 against that of 3 : 1 might be used to compare the stabilising effects of the ketonic and the ester group on the intermediate radicals, *i.e.*, the former group is roughly 3·3 times as stabilising as the latter. This comparison of isomer ratios therefore constitutes an intermolecular comparison of relative stabilising capacities, in pursuance of which the addition of heptanal to ethyl ββ-dimethylacrylate and of butanal to ββ-dimethylacrylic acid (I; X = $\mathrm{CO_2H}$) and to the nitrile (I; X = CN) have been investigated, benzoyl peroxide being used as the catalyst.

$\mathrm{Me_2C{:}CHX}$

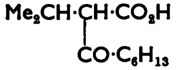
(I)

$\mathrm{Me_2C(COPr^n)\cdot CH_2X}$ $\mathrm{Me_2CH\cdot CH(COPr^n)X}$

(II) X = Ac (III)
(IV) X = $\mathrm{CO_2Et}$ (V)
(VI) X = $\mathrm{CO_2H}$ (VII)
(VIII) X = CN (IX)



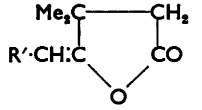
$\mathrm{Me_2C(CO\cdot C_6H_{13})\cdot CH_2\cdot CO_2H}$ (X)



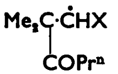
$\mathrm{Me_2CH\cdot CH(CO\cdot C_6H_{13})\cdot CO_2H}$ (XI)

$\mathrm{Me_2CH\cdot CH_2\cdot COR}$

(XII) R = $\mathrm{Pr^n}$
(XIII) R = $\mathrm{C_6H_{13}}$

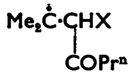


(XIV) R′ = Et
(XV) R′ = $\mathrm{C_5H_{11}}$



$\mathrm{Me_2C(COPr^n)\cdot\dot{C}HX}$

(XVI*a*) X = Ac
(XVII*a*) X = CN



$\mathrm{Me_2\dot{C}\cdot CH(COPr^n)X}$

(XVI*b*) X = Ac
(XVII*b*) X = CN

Addition of butanal to ethyl ββ-dimethylacrylate afforded, in good yield, a mixture of the isomeric esters (IV) and (V) (correct elemental analysis but wide boiling range), accompanied by only negligible quantities of polymer. To estimate the proportion of each ester present the mixture was hydrolysed with boiling aqueous alkali, giving the γ-keto-acid (VI) and the neutral ketone (XII) in a molar ratio of 2·7 : 1. The latter substance must have resulted from the β-keto-acid (VII) through decarboxylation, and thus the adduct mixture contained the γ- and the β-keto-ester in a ratio of approximately 3 : 1. The γ-keto-acid was found to be stable at 160°, but was converted into the unsaturated lactone (XIV) by hot acetic anhydride.

Heptanal and the same acrylic ester gave a mixture of adducts which on similar treatment with alkali yielded the unsaturated lactone (XV) and the neutral ketone (XIII) in a molar ratio of 2·9 : 1. The former was undoubtedly derived from the γ-keto-acid (X), probably by enolisation followed by dehydration during distillation, whereas the latter must have been the decarboxylated product of the β-keto-acid (XI). The ratio of γ-keto-esters is therefore again approximately 3 : 1. As before, only small quantities of polymer were encountered.

ββ-Dimethylacrylic acid gave with butanal the acid (VI) and the ketone (XII) in a molar ratio of 2·8 : 1. An unidentified neutral fraction of a wide boiling range was also produced, together with a little undistillable material.

From the addition of butanal to ββ-dimethylacrylonitrile only one adduct, (VIII), was obtained (52% yield), fractionation failing to reveal any of the isomer (IX). The homogeneity of the product was confirmed by (*a*) its failure to give any of the usual tests for a

---

[1] Patrick, *J. Org. Chem.*, 1952, **17**, 1269.

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

[3] Kharasch, Urry, and Kuderna, *J. Org. Chem.*, 1949, **14**, 248; see also Patrick, *ibid.*, 1952, **17**, 1009.

keto-enol system to which the latter isomer would be expected to respond, and (*b*) its alkaline hydrolysis in a high yield (86%) to the γ-keto-acid (VI), accompanied by only negligible quantities of neutral material, which was not the ketone (XII). Absence of the nitrile (IX) is thus clearly demonstrated. Polymeric products, however, were present in considerable quantities.

The isomer ratios when X = Ac, $CO_2Et$, $CO_2H$, and CN are thus 10 : 1, 3 : 1, 3 : 1, and ∞ : 1 respectively. The results obtained for the ketonic and ester substituents more than confirm the conclusion reached in Part I, *viz.*, CO > $CO_2Et$; indeed, they afford a quantitative measure of the stabilising influences. Comparison of these ratios in other cases is unfortunately less decisive. It will be appreciated that, should by-products, polymeric or otherwise, of unknown precise origin, be formed to a significant extent, the isomer ratios give at best only the order of stabilising influence. This is the case with ββ-dimethylacrylic acid in which unidentified by-products are found in quantities comparable with those of the minor isomer. Consequently, although when compared with the ketonic group in mesityl oxide (ratio 10 : 1) the carboxyl group is clearly of a lower order of stabilising power, a comparison with the ester group (ratio also 3 : 1) is much less significant and gives the two substituents as probably of the same order of stabilising capacity. In Part I, the relation $CO_2Et > CO_2H$ was based on the addition of butanal to ethyl hydrogen maleate, and, since (*a*) the yield of the main adduct was just under 50%, and (*b*) the possibility of ester-interchange under the experimental conditions could not be excluded, it seems desirable to defer a final assessment of these groups.

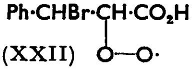
Again, in the addition of butanal to ββ-dimethylacrylonitrile, although the adduct (VIII) was formed to the complete exclusion of the isomer (IX), polymeric material was produced to the extent of 30% by weight of the total product. At first sight this might seem to render infeasible any comparison of the isomer ratio with other cases, since these polymers could have been derived from the less stable radical (XVII*b*), by dimerisation, or by telomerisation, *i.e.*, by attack on another molecule of the acrylonitrile. However, this is rendered improbable by the following consideration. If the polymer were produced by dimerisation of the intermediate radicals, it would be expected that the more stable radical, *i.e.*, (XVII*a*) [since (VIII) was the main adduct], would have been the main precursor,[4] and not (XVII*b*). On the other hand, if telomerisation were the mechanism involved, then, unless the unlikely assumption is made that *all* of the radicals (XVII*b*) formed reacted preferentially with the acrylonitrile, rather than attacked the butanal present in excess to give the isomer (IX), the complete absence of this isomer can be explained only by assuming that its precursor [the radical (XVII*b*)] was formed only to a very small extent if at all. It seems reasonable therefore to evaluate the cyano-group as possibly of a somewhat higher, or more probably of roughly the same, order of stabilising influence as the ketonic group.

$\mathrm{Me_2\dot{C}{\cdot}CO_2Et}$ (XVIII)

$\mathrm{Me_2\dot{C}{\cdot}CN}$ (XIX)

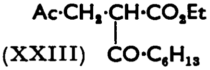
$\mathrm{Ph{\cdot}CHBr{\cdot}\dot{C}H{\cdot}CO_2H}$ (XX)

$\mathrm{Ph{\cdot}\dot{C}H{\cdot}CHBr{\cdot}CO_2H}$ (XXI)



$\mathrm{Ph{\cdot}CHBr{\cdot}\underset{O-O\cdot}{\underset{|}{C}}H{\cdot}CO_2H}$

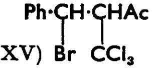
(XXII)



$\mathrm{Ac{\cdot}CH_2{\cdot}\underset{CO{\cdot}C_6H_{13}}{\underset{|}{C}}H{\cdot}CO_2Et}$

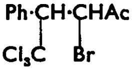
(XXIII)

$\mathrm{Ac{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}C_6H_{13}}$ (XXIV)



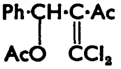
$\mathrm{Ph{\cdot}\underset{Br}{\underset{|}{C}}H{\cdot}\underset{CCl_3}{\underset{|}{C}}HAc}$

(XXV)



$\mathrm{Ph{\cdot}\underset{Cl_3C}{\underset{|}{C}}H{\cdot}\underset{Br}{\underset{|}{C}}HAc}$

(XXVI)



$\mathrm{Ph{\cdot}\underset{AcO}{\underset{|}{C}}H{\cdot}\underset{CCl_2}{\underset{\|}{C}}{\cdot}Ac}$

(XXVII)

By this approach we therefore arrive at the following scale of relative stabilising capacities: $CN \approx CO > CO_2Et \approx CO_2H$. And since, from Part I, Ph > CN and $CO_2H > Me$, we have $Ph > CN \approx CO > CO_2Et \approx CO_2H > Me$. This scale provides a rational

---

[4] Cf. Huang and Lee, *J.*, 1954, 2570.

basis on which the properties of certain free radicals and the course of many homolytic reactions can be explained, and in some cases, predicted. For example, the much greater tendency [5] of the ethoxycarbonylalkyl radical (XVIII) to disproportionate compared with the cyanoalkyl radical (XIX) is explicable in terms of the greater stabilising effect of the cyano-group. In the oxidation of cinnamic acid in the presence of atomic bromine, Brown and Daniels [6] consider the radical (XX) to be initially involved, which then with oxygen gives rise to the peroxidic radical (XXII). Waters,[7] on the other hand, prefers the intermediate (XXI), rather than (XX), although both of these satisfactorily account for the formation of the reaction products. From the now known relative stabilising influences of the phenyl and the carboxyl group, Waters's formulation is clearly correct.

Again, considering the stabilising effects of the ketonic and the ester group, the addition of heptanal to ethyl β-acetylacrylate would be expected to lead to the ester (XXIII). This has been shown to be the case by hydrolysis of the adduct, which being a β-keto-ester underwent decarboxylation as well as hydrolysis to give the 1 : 4-diketone (XXIV), identified as the pyrrole derivative formed with semicarbazide (cf. Part I). Similarly, the addition product from bromotrichloromethane and benzylideneacetone would in all probability have the structure (XXV). Although attempts to degrade the adduct to known products were not successful, this structure for it is consistent with its complete inertness towards thiourea, which would be difficult to explain on the basis of the alternative structure (XXVI), inasmuch as α-halogenoketones (*e.g.*, chloroacetone, phenacyl bromide) are known to react readily with thiourea to form aminothiazoles.[8] The unsuccessful degradative studies include (i) catalytic hydrogenation, (ii) reduction with zinc and magnesium, and (iii) treatment with potassium acetate in acetic acid, which converted the product into a partially dechlorinated substance, probably (XXVII).

Finally, in the homolytic bromination by *N*-bromosuccinimide, a process now known to result in substitution by bromine at the carbon atom which becomes the radical centre in the intermediate,[9] a substance such as β-phenylpropionic acid would be expected, in view of the dominant stabilising power of the benzene ring over the carboxyl group, to be brominated in the β- rather than the α-position. This has indeed been proved to be the case. Conversely, selective bromination by *N*-bromosuccinimide of substances containing two functional groups X and Y, such as $X{\cdot}[CH_2]_x{\cdot}Y$, and devoid of steric complications, should furnish yet another approach to the comparison of the stabilising capacities of such groups. Work in this direction is in progress.

## EXPERIMENTAL

*Addition of Butanal to Ethyl* ββ-*Dimethylacrylate*.—Benzoyl peroxide (2·4 g.) was added in three portions during 24 hr. to a mixture of butanal (42 g.) and ethyl ββ-dimethylacrylate (15 g.; $n_D^{23}$ 1·4350) at 80° under nitrogen. Heating was continued for 24 hr. more, after which unchanged butanal was removed by distillation followed by co-distillation with benzene. The product was taken up in ether, washed 5 times with 5% aqueous sodium hydrogen carbonate, once with water, dried ($MgSO_4$), and recovered. Distillation gave fractions (i) b. p. *ca.* 50°/1 mm., $n_D^{23}$ 1·4260 (1 g.), and (ii) b. p. 90—94°/1 mm., $n_D^{23}$ 1·4317 (14·4 g., 63%), and a residue, $n_D^{23}$ 1·4534 (2 g.). A portion of the main fraction (ii) was distilled, giving mixed esters, b. p. 80° (bath)/0·3 mm., $n_D^{23}$ 1·4311 (Found: C, 66·45; H, 10·3. Calc. for $C_{11}H_{20}O_3$: C, 66·0; H, 10·1%). Another portion (5·5 g.) was refluxed with 10% aqueous sodium hydroxide (30 c.c.) for 7·5 hr. The solution then being homogeneous, it was extracted with ether (4 × 25 c.c.), and the extract washed once with water. This washing, combined with the alkali fraction, was concentrated under partially reduced pressure to *ca.* 15 c.c. (in another experiment in which this was omitted troublesome emulsions were encountered in the subsequent extraction),

---

[5] Bickel and Waters, *Rec. Trav. chim.*, 1950, **69**, 312, 1490.

[6] Brown and Daniels, *J. Amer. Chem. Soc.*, 1940, **62**, 2821.

[7] Waters, " Chemistry of Free Radicals," 1946, Oxford Univ. Press, p. 177.

[8] *E.g.*, Traumann, *Annalen*, 1888, **249**, 38; King and Hlavacek, *J. Amer. Chem. Soc.*, 1950, **72**, 3722.

[9] Bloomfield, *J.*, 1944, 114.

then acidified with concentrated hydrochloric acid, and the acid which separated taken up in much ether and washed once with a little water. Distillation gave mainly 3 : 3-*dimethyl*-4-*oxoheptanoic acid*, b. p. 104°/0·5 mm. (2·77 g.), $n_D^{24}$ 1·4480 (Found : C, 62·6, 62·85; H, 9·6, 9·3. $C_9H_{16}O_3$ requires C, 62·8; H, 9·4%), there being practically no residue. The 2 : 4-*dinitrophenylhydrazone*, yellow needles from aqueous ethanol, melted at 135—136° (Found : N, 15·7. $C_{15}H_{20}O_6N_4$ requires N, 15·9%) ; the *semicarbazone*, needles from ethanol, had m. p. 198° (Found : N, 18·05. $C_{10}H_{19}O_3N_3$ requires N, 18·3%). The neutral fraction obtained as above was practically pure *iso*butyl *n*-propyl ketone, b. p. 154—158°/755 mm. (0·73 g.), which was further distilled (b. p. 155°/755 mm., $n_D^{24}$ 1·4098) (Found : C, 74·6; H, 12·4. Calc. for $C_8H_{16}O$ : C, 74·9; H, 12·6%) (semicarbazone, m. p. 122—123°). Fournier [10] reports b. p. 155°/750 mm. and m. p. 123—124°, respectively. This ketone corresponds to 1·06 g. of the decarboxylated β-keto-acid. The ratio of the γ- : β-keto-acids is hence 2·6 : 1.

In another hydrolysis 6·0 g. of the ester mixture gave 3·84 g of the γ-keto-acid and 1·01 g. of the ketone. The ratio is therefore 2·8 : 1.

The above γ-keto-acid was stable at 160° for 2 hr., decomposing only to a small extent to the unsaturated lactone. Heating with an equal volume of acetic anhydride at 100° for 4 hr., however, converted it into 4-*hydroxy*-3 : 3-*dimethylhept*-4-*enoic lactone*, b. p. 60° (bath)/0·5 mm., $n_D^{24}$ 1·4568 (Found : C, 70·6; H, 9·0. $C_9H_{14}O_2$ requires C, 70·1; H, 9·15%), which decolorised bromine in chloroform instantly and dissolved in 20% aqueous sodium hydroxide only after *ca.* 15 minutes' heating.

*Addition of Butanal to ββ-Dimethylacrylic Acid.*—The product from the acid (25·0 g.), butanal (110 g.), and benzoyl peroxide (4·8 g.) was diluted with ether and extracted with 20% aqueous sodium carbonate (5 × 30 c.c.), thus giving an aqueous solution A and an ethereal solution B. Solution A was washed with ether, acidified with concentrated hydrochloric acid, then concentrated to half its volume by distillation at 190 mm. (ββ-dimethylacrylic acid readily steam-distils under these conditions, while 3 : 3-dimethyl-4-oxoheptanoic acid does not). No dimethylacrylic acid was recovered. The solution was then extracted with ether, and the ethereal extract dried and finally distilled, giving fractions (i) b. p. 112—116°/2 mm. (8·0 g.), and (ii) 3 : 3-dimethyl-4-oxoheptanoic acid, b. p. 116—118°/2 mm., $n_D^{24}$ 1·4498 (16 g.) (semicarbazone, m. p. and mixed m. p. 198°), and a residue (*ca.* 1 g.). Fraction (i) partially crystallised, and the supernatant liquid (4·3 g.), which was decanted, was shown to contain 88% (4·0 g.) of the same γ-keto-acid by a comparison of the yields of semicarbazone formed by a pure sample under the same conditions (2·5 g. from 2·0 g. acid). The total yield of the γ-keto-acid was therefore 20·0 g. The solid which separated from (i) was benzoic acid (*ca.* 2·7 g. ; m. p. and mixed m. p. after recrystallisation from light petroleum).

Solution B was dried and concentrated, and after fractionation gave (i) *sec.*-butyl *n*-propyl ketone (5·8 g.), b. p. 154—159°/760 mm., $n_D^{23}$ 1·4120 (semicarbazone, m. p. and mixed m. p. 123°), (ii) material, b. p. 55—104°/1 mm., $n_D^{23}$ 1·4464 (1·4 g.), which did not react with semicarbazide and was not further investigated, (iii) more 3 : 3-dimethyl-4-oxoheptanoic acid (1·7 g.), b. p. 106—118°/1 mm., $n_D^{23}$ 1·4496, soluble in aqueous sodium carbonate (semicarbazone, m. p. and mixed m. p. 196—197°), and (iv) an undistillable residue (2·7 g. ; bath up to 160°/1 mm.).

The yield of γ-keto-acid is thus 21·7 g., against a computed yield of 7·8 g. of the decarboxyled β-keto-acid, giving a ratio of 2·8 : 1 (total yield of keto acids : 69%).

*Addition of Heptanal to Ethyl ββ-Dimethylacrylate.*—The reaction mixture from the acrylate (19·3 g.), heptanal (85 g.), and benzoyl peroxide (2·9 g.), after removal of excess of aldehyde under reduced pressure and of benzoic acid, gave on distillation fractions (i) b. p. 94—98°/0·5 mm. (2 g.) and (ii) 98—105°/0·5 mm. (23·5 g. ; 65%), $n_D^{23}$ 1·4382, and a residue (3·0 g.). A portion (11·4 g.) of fraction (ii) was refluxed with 10% sodium hydroxide solution (60 c.c.) for 8 hr., and the products were worked up as before, giving (*a*) *iso*butyl *n*-hexyl ketone, b. p. 160° (bath)/7 mm. (the ketone froths uncontrollably when vacuum-distilled with a capillary leak, and is best distilled evaporatively), $n_D^{23}$ 1·4241 (1·6 g.) (Found : C, 77·6; H, 13·1. Calc. for $C_{11}H_{22}O$ : C, 77·6; H, 13·0%), and (*b*) 4-*hydroxy*-3 : 3-*dimethyldec*-4-*enoic lactone*, b. p. 99—100°/0·5 mm., $n_D^{23}$ 1·4590 (5·4 g.) (Found : C, 73·3, 73·2; H, 10·2, 10·1. $C_{12}H_{20}O_2$ requires C, 73·4; H, 10·3%). The lactone was insoluble in cold 20% aqueous sodium hydroxide, but dissolved slowly therein when warmed ; it decolorised bromine instantly in chloroform. Heating it with a solution of semicarbazide in aqueous alcohol in presence of sodium acetate for 15

---

[10] Fournier, *Bull. Soc. chim. France*, 1910, **7**, 839.

min. and storage for 48 hr. gave 3 : 3-*dimethyl*-4-*semicarbazonodecanoic acid*, needles (from aqueous ethanol), m. p. 147—150° (Found : C, 57·4; H, 9·35; N, 15·4. $C_{13}H_{25}O_3N_3$ requires C, 57·5; H, 9·3; N, 15·5%). The yield of lactone corresponds to 5·9 g. of the γ-keto-acid, and that of the ketone to 2·0 g. of the decarboxylated β-keto-acid, giving a ratio of 2·9 : 1 (yield, 79%).

Hydrolysis of the ester mixture with 10% aqueous-ethanolic (1 : 1) potassium carbonate was incomplete (56% unchanged) after 7·5 hr.

Addition of heptanal (38 g.) to the acrylate (7·2 g.) by heating with di-*tert*.-butyl peroxide (0·88 g., 10 moles %) at 125—135° for 46 hr. gave on distillation an ester mixture, b. p. 76—98°/1 mm. (8·0 g.), $n_D^{23}$ 1·4352, and a large undistillable residue (15·4 g., bath up to 175°/1 mm.).

*Addition of Butanal to* ββ-*Dimethylacrylonitrile*.—The product obtained by heating at 75° for 26 hr. butanal (94 g., 1·3 moles), the nitrile (17·0 g., 0·21 mole; b. p. 65°/56 mm., $n_D^{21}$ 1·4332; see Felton and Orr [11]), and benzoyl peroxide (6·0 g., 0·025 mole; added in 3 portions during the first 18 hr.) was carefully fractionated through a 15 cm. Vigreux column, the following fractions being collected : (i) b. p. 50—60°/95 mm. (2·95 g.); (ii) b. p. 61°/45 mm., $n_D^{21}$ 1·4342 (3·5 g.); (ii) b. p. 71—73°/2 mm., $n_D^{21}$ 1·4395 (8·21 g.); and (iv) b. p. 73°/2 mm., $n_D^{21}$ 1·4398 (2·56 g.). The Vigreux column was then replaced by an ordinary distilling head (*ca.* 4 cm.) and distillation continued to give fraction (v), b. p. 99—104°/2 mm., $n_D^{21}$ 1·4561 (0·50 g.), a pale, somewhat viscous liquid, and (vi) an undistillable residue (5·15 g.) (bath up to 155°). Fraction (i) on distilling at atmospheric pressure through a 5 cm. Vigreux column gave benzene (0·7 g. from benzene added to co-distil with excess of butanal), the remainder being mostly unchanged ββ-dimethylacrylonitrile, which, together with fraction (ii), made a total of 5·8 g. of recovered material. Fractions (iii) and (iv) were both 3 : 3-*dimethyl*-4-*oxoheptanonitrile* (10·8 g., 52% calc. on the nitrile consumed) (Found : C, 70·6; H, 9·8; N, 9·3. $C_9H_{15}ON$ requires C, 70·55; H, 9·9; N, 9·1%). It was insoluble in 20% aqueous potassium hydroxide and did not decolorise bromine, or give a colour with ferric chloride. Its *semicarbazone*, needles from aqueous ethanol, had m. p. 183—185° (Found : N, 26·55. $C_{10}H_{18}ON_4$ requires N, 26·65%).

*Hydrolysis*. The above adduct (9·0 g.) was boiled under an efficient reflux condenser with 15% aqueous sodium hydroxide (75 c.c.) for 9 hr. Next day the mixture was thoroughly extracted with ether (4 × 50 c.c.). The ethereal extract was washed with water once, dried, and on evaporation gave very small quantities of a brown oil (0·18 g.), which did not react with semicarbazide. The aqueous fraction was concentrated under partially reduced pressure to *ca.* 30 c.c., acidified under cooling with concentrated hydrochloric acid, and the acid so precipitated taken up in much ether, dried, and concentrated, giving 3 : 3-dimethyl-4-oxoheptanoic acid (crude, 8·7 g., 86%) which was distilled, b. p. 106—108°/1 mm. (6·5 g.), $n_D^{20}$ 1·4491 (semicarbazone, m. p. 200°, alone or mixed with the sample obtained previously).

*Addition of Heptanal to Ethyl* β-*Acetylacrylate* (with SIM WONG KOOI).—The acrylate (16·6 g.), heptanal (79 g.), and benzoyl peroxide (4 × 0·6 g.), when heated at 70° for 7 hr. and 85° for 1 hr., gave on distillation *ethyl* 2 : 5-*dioxoundecane*-4-*carboxylate*, b. p. 119—121°/1 mm., $n_D^{24}$ 1·4481 (12·6 g., 42%) (Found : C, 65·5, 65·5; H, 9·3, 9·4. $C_{14}H_{24}O_4$ requires C, 65·6; H, 9·4%). The adduct was soluble in 30% sodium hydroxide solution, decolorised bromine instantly in carbon tetrachloride, and gave a reddish-violet colour with ferric chloride. The *semicarbazone*, leaflets from ethanol, had m. p. 184—185° (Found : N, 14·0. $C_{15}H_{25}O_3N_3$ requires N, 14·2%). A sample of the adduct (4·5 g.) was hydrolysed by potassium carbonate (5 g.) in boiling water (30 c.c.) and ethanol (20 c.c.) for 8 hr. Ethanol was removed under reduced pressure, and the neutral product taken up in ether and evaporatively distilled, to give undecane-2 : 5-dione, b. p. 90° (bath)/0·5 mm., $n_D^{24}$ 1·4430 (*ca.* 2 g.), identified as (2-methyl-5-hexyl-1-pyrryl)urea which it formed readily with semicarbazide, m. p. 152—153° (Found : N, 18·9. $C_{12}H_{21}ON_3$ requires 18·8%).

*Addition of Bromotrichloromethane to Benzylideneacetone*.—Benzoyl peroxide (8 g., 24 mole %) was added in 4 portions during 12 hr. to benzylideneacetone (20 g.) and bromotrichloromethane (160 g.) at 60—65° under nitrogen. Heating was continued for 12 hr. more, the last hr. being at 90°. After removal of benzoic acid in aqueous sodium hydrogen carbonate, and excess of bromotrichloromethane under reduced pressure, addition of methanol and chilling caused the separation of 4-*bromo*-4-*phenyl*-3-*trichloromethylbutan*-2-*one* which was filtered off. It had m. p. 81—86° (20·5 g., 43%), raised to 95—97° on recrystallisation from methanol, from which it was obtained as needles (Found : C, 38·4; H, 3·1; Br, 23·2. $C_{11}H_{10}OBrCl_3$ requires C, 38·3; H, 2·9; Br, 23·2%). A small quantity of a sparingly soluble solid, m. p. 262° (decomp.) (0·25 g.),

---

[11] Felton and Orr, *J.*, 1955, 2172.

was separated during the first recrystallisation, but was not further investigated. The filtrate was concentrated to a brown viscous oil (27 g.), and was heated with potassium acetate (27 g.) in glacial acetic acid (120 c.c.) at 80° for 20 hr. and then at 100° for 2 hr. After removal by distillation under reduced pressure of most of the acetic acid, the mixture was poured into water and neutralised with sodium carbonate, and the product taken up in ether, washed with water, and dried. Distillation then gave unchanged benzylideneacetone, $n_D^{24}$ 1·5850 (*ca.* 1 g.) (semicarbazone, m. p. and mixed m. p. 182—185°), and *4-acetoxy-3-dichloromethylene-4-phenylbutan-2-one* (4·0 g.), b. p. 122—126°/2 mm., $n_D^{24}$ 1·5420 (the refractive index is slightly too high owing to admixture with traces of benzylideneacetone. This was found to be the case whenever dehydrobromination was carried out on material containing the starting material. The solid adduct, however, gave a product with constant value for the refractive index; see below) (Found: C, 54·5; H, 4·3; Cl, 24·6. $C_{13}H_{12}O_3Cl_2$ requires C, 54·4; H, 4·2; Cl, 24·7%). Its *semicarbazone*, which crystallised from aqueous ethanol in needles, melted at 182° (Found: C, 49·3, 49·3; H, 4·2, 4·6; N, 12·0, 11·9. $C_{14}H_{15}O_3N_3Cl_2$ requires C, 48·9; H, 4·4; N, 12·2%). There was an undistillable residue (10 g.). The second fraction above (4·0 g.) corresponds to a further yield of at least 5 g. of the solid adduct, bringing the total yield to 57% or higher, based on the benzylideneacetone consumed.

Use of only 10 mole % of benzoyl peroxide and heating for 10 hr. gave 23% of unchanged benzylideneacetone and 45% of the adduct.

*Degradation.* (i) Reaction with potassium acetate. The above adduct (3 g.; m. p. 93—95°) was heated with potassium acetate (4 g.) in glacial acetic acid (20 c.c.) as described above. Distillation of the product gave the same acetoxybutanone, b. p. 140° (bath)/1 mm. (1·9 g., 76%), $n_D^{24}$ 1·5350 (Found: C, 54·45; H, 4·4; Cl, 25·0%). Its semicarbazone had m. p. 182—184°, alone or mixed with the sample obtained as above. Further distillation gave fractions of the same refractive index.

Treatment with only one mol. of potassium acetate in the same way gave a partially debrominated and partially dechlorinated product.

(ii) Hydrogenation. (*a*) The adduct, in ethanol in the presence of 10% palladised charcoal and magnesium oxide ("AnalaR") absorbed 1·1 mol. of hydrogen in 10 min., giving a hygroscopic colloidal solid. Attempts to crystallise this from the usual organic solvents failed. An attempt to distil it *in vacuo* also failed, much decomposition occurring in the final stages of heating (bath up to 160°/0·5 mm.). (*b*) With Raney nickel (of proved activity) in ethanol containing pure pyridine, there was no uptake of hydrogen. (*c*) With Adams catalyst in ethanol, two mols. of hydrogen were taken up in 20 min., giving an oil which did not produce any crystalline material after chromatography on alumina (light petroleum–benzene).

(iii) Reaction with thiourea. The adduct and thiourea, after 2·5 hr. under reflux in ethanol, were both recovered quantitatively.

(iv) Reduction with a mixture of zinc and magnesium powder in ethanol and 50% hydrochloric acid gave on distillation a mixture of halogen-containing substances and *ca.* 30% of polymer.

*Wohl–Ziegler Bromination of* β*-Phenylpropionic Acid* (with PEARL WILLIAMS).—*N*-Bromosuccinimide (recrystallised from hot water; 2·86 g., 0·016 mole) was added to a solution of β-phenylpropionic acid (3·1 g., 0·021 mole; m. p. 49—50°) in carbon tetrachloride (*ca.* 10 c.c.; "AnalaR") and the mixture illuminated under nitrogen with a 100-w incandescent lamp. The solution, on being boiled, became pale yellow, but little or no bromine or hydrogen bromide was evolved. After 10 minutes' refluxing the mixture became homogeneous. It was cooled slightly, and the precipitated succinimide filtered off. The filtrate was further cooled, the solid (4·5 g.) which separated consisting mainly of β-bromo-β-phenylpropionic acid and a little succinimide was collected, and dissolved in chloroform, and the solution was washed twice with water, dried, and concentrated to a small volume. On addition of hot carbon tetrachloride and cooling, pure β-bromo-β-phenylpropionic acid crystallised; it had m. p. 141—142° (lit., 137°) (2·1 g., 58% calc. on the *N*-bromosuccinimide used) (Found: C, 46·95; H, 3·9. Calc. for $C_9H_9O_2Br$: C, 47·2; H, 3·9%).

UNIVERSITY OF MALAYA, SINGAPORE.

[*Received, October 8th,* 1956.]