C.—Investigations of the Olefinic Acids. Part V. The Influence of Bases on the Condensation of Aldehydes and Malonic Acid, and a Note on the Knoevenagel Reaction.

By Stanley Edward Boxer and Reginald Patrick Linstead.

The reaction of aldehydes with malonic acid in the presence of organic bases is of considerable value for the preparation of unsaturated acids and it is a matter for surprise that neither the course of the reaction under various conditions nor its mechanism is known with certainty. The fairly extensive literature on this reaction relates in the main to its application for preparative purposes by two general methods. That originally due to Knoevenagel (G.P. 97735, 1896), in which *primary and secondary bases* are used as catalysts, was at first limited to aromatic aldehydes but was extended to the aliphatic series in 1902 (G.P. 156560). Priority for the introduction of the second method, involving the use of *pyridine* as catalyst, must be assigned to Verley (*Bull. Soc. chim.*, 1899, **21**, 143) and not, as is commonly done, to Doebner, who subsequently extended its use (*Ber.*, 1900, **33**, 2140; 1901, **34**, 53; 1902, **35**, 1136, 2137). Later workers have generally preferred this modification for synthetic purposes (compare, *e.g.*, Harding and Weizmann, J., 1910, **97**, 299), although the introduction of a small quantity of a secondary base into the pyridine reaction mixture is often considered advantageous (Haworth, Perkin, and Rankin, J., 1924, **125**, 1693).

The conditions necessary for the formation of three only of the possible types of reaction product are known with certainty. (i) The pyridine method gives good yields of acrylic acids (type I) in a high state of purity and free from stereoisomerides (von Auwers, *Annalen*, 1923, **432**, 46). (ii) Under Knoevenagel's conditions, the use of an excess of malonic acid leads to the formation of glutaric acids (II) (*Ber.*, 1898, **31**, 2585; 1902, *loc. cit.*). (iii) Substances of the type of benzylidenemalonic acid (III; R = Ph) can readily be prepared from aromatic aldehydes if precautions are taken to avoid the loss of carbon dioxide (Knoevenagel, *Ber.*, 1898, **31**, 2596; G.P. 164296, 1904).

(I.) $CH_2R{\cdot}CH{:}CH{\cdot}CO_2H$ $CH_2R{\cdot}CH(CH_2{\cdot}CO_2H)_2$ (II.)

(III.) $CHR{:}C(CO_2H)_2$ $CHR{:}CH{\cdot}CH_2{\cdot}CO_2H$ (IV.)

In the aliphatic series, unsaturated malonic acids (III) have been isolated in the pure state only from complex or unsaturated aldehydes (*e.g.*, citral; Verley, *loc. cit.*: crotonaldehyde; Riedel, *Annalen*, 1908, **361**, 89).* The formation of βγ-olefinic acids (IV) has also occasionally been noted; for instance, von Auwers (*loc. cit.*), from physical measurements, deduced their presence in the products obtained in pyridine condensations at 100°. Phenylacetaldehyde appears to be unique in yielding almost pure βγ-acid (IV; R = Ph) under all conditions of condensation (Vorländer, *Annalen*, 1906, **345**, 244; Linstead and Williams, J., 1926, 2735). The general conditions necessary for the production of βγ-acids were still uncertain when the present work was begun, but during its progress Zaar published an account (*Ber. Schimmel*, 1929, 299) of the preparation of Δ^{β}-*n*-octenoic acid from heptaldehyde, piperidine or diphenylamine being used as catalyst, and stated that reactions catalysed by secondary and by tertiary bases yield βγ- and αβ-acids respectively.

The lack of agreement in the results of earlier workers suggested the need for further experimental study of this reaction, particularly in the aliphatic series. The present paper gives the results obtained by the condensation of one aldehyde (*n*-butaldehyde) with malonic acid, bases of every possible type, strong or weak, primary, secondary, or tertiary, being used as catalysts. Two series of experiments

---

* Vogel (J., 1927, 1985) describes the production of "ethylidenemalonic acid" (m. p. 82°) from acetaldehyde and malonic acid in presence of pyridine–piperidine, and refers to a paper (Kommenos, *Annalen*, 1883, **218**, 165) which gives the preparation of an acid of similar m. p. from the same reagents by means of acetic anhydride as condensing agent. The reference is, however, erroneous: Kommenos showed his acid to be β-methylglutaric ("ethylidenediacetic") acid and it is reasonably certain that Vogel's compound was the same, particularly in view of the low density of his ethyl ester.

were carried out, in one a small quantity of the base being used, and in the other a molecular quantity or an excess. These correspond broadly with the two general methods used in the past for condensations of this type. Reaction was allowed to take place first at room temperature and then at 100°, the only difference in procedure being that in the experiments with a trace of catalyst the products were distilled in steam before isolation.

As a result of the heating at 100° decarboxylation accompanied condensation and the acid products were mixtures of the monobasic unsaturated acids; in this case, the Δ^{α}- and the Δ^{β}-*n*-hexenoic acid (I and IV; R = Et). Separate reference is made later to experiments on the isolation of glutaric acids and unsaturated malonic acids. The compositions of the mixtures of hexenoic acids were found by determinations of the equivalent and of the iodine addition, by their melting points, alone and in admixture with the pure αβ- and βγ-acids, by optical measurements, and in some cases by the preparation of derivatives. The more important results obtained are summarised in Table I.

TABLE I.

Condensation of *n*-Butaldehyde and Malonic Acid.

Base.	Yield † %.	M. p.	Iodine addition at 20°.	% βγ-Acid.
(*A*) Base in small amount.				
Pyridine	21	0°	46·9	79
Piperidine	21	5	50·2	86
Triethanolamine (pure)	10	9—10	54·0	97
Dimethylaniline	14	7—8	52·5	92
Diphenylamine *	12	7	51·0	88
Quinoline	10	3	42·4	68
Ammonium chloride	14	4—5	43·2	70
Aniline hydrochloride *	14	7	53·2	94
(*B*) Base in molecular amount or in excess.				
Pyridine	*ca.* 75—82 ‡	—	—	*ca.* 2—5 ‡
Piperidine	10	3—4	44·5	73
Triethanolamine	37	12	56·1	100
Dimethylaniline	23	10	56·1	100
Quinoline	19	6—7	48·2	80

* Aniline itself gave poor results by both methods, as did diphenylamine by the second.

† Yield of mixed hexenoic acids of correct boiling range and equivalent.

‡ The highest yields are obtained by prolonging the time of heating, but this increases the proportion of βγ-acid.

These results show many features of interest. In the first place, with the exception of pyridine, all the bases tried yield mainly βγ-acid and the amount of the base has little influence on the nature of the product. The generalisation of Zaar (*loc. cit.*), which attempts to correlate the nature of the product with the order of the base, is obviously incorrect. The well-established use of pyridine for the preparation of αβ-acids represents an *abnormal* reaction with respect to the general action of bases; but the use of *traces* of pyridine gives a poorer yield of a product which is mainly βγ-acid. The determining influence of an *excess* of pyridine on the nature of the product is clearly shown by the fact that a mixture of a large amount of this base and a trace of piperidine yields nearly pure αβ-acids (*e.g.*, Goldberg and Linstead, J., 1928, 2343). This extraordinary abnormality of pyridine appears to be specific; it is not shared by other tertiary bases (*e.g.*, triethanolamine), nor by those of approximately the same strength (*e.g.*, dimethylaniline), nor even by quinoline, which has the same general chemical characteristics.

The formation of βγ-acid in all the other condensations cannot be attributed to the equilibrating action of bases on the αβ-acid, as this would be expected to be slow and would in any case give an equilibrium on the αβ-side. Neither is it possible that the steam distillation used in the experiments with small amounts of bases could be of major importance in determining the position of the double bond, as such distillation was started only when all the carbon dioxide had been evolved and hence when all the monobasic acid had been formed.

The condensations using small amounts of dimethylaniline and triethanolamine (ββ′β″-trihydroxytriethylamine) give reasonable yields of βγ-acid remarkably free from its isomeride, and the availability and low cost of the second of these bases led us to develop its use for the preparation of Δ^{β}-*n*-hexenoic acid in quantity. This process is much more rapid and economical than any of those previously used and this acid is now the most readily obtainable βγ-olefinic acid. The properties of the acid so prepared and those of samples of Δ^{β}-*n*-hexenoic acid isolated from the equilibrated αβ-acid (Eccott and Linstead, J., 1929, 2159) are compared in Table II, and suggest that the original "solid" βγ-acid contained some 5% of the αβ-isomeride.

TABLE II.

Properties of Δ^{β}-*n*-Hexenoic Acids.

Acid sample.	B. p. /mm.	M. p.	Iodine addition at *t*°.	$d^{t°}_{4°}$.	$n^{t°}_{D}$.	$[R_L]_D$.	M. p. of *p*-toluidide.
From equilibrium mixture:							
Original sample (*loc. cit.*)	105°/13	4—5°	46·7	0·9626/14°	1·4397/14°	31·23	95°
New preparation	111/19	5	52·0/20	0·9621/19	1·4391/19	31·23	—
Triethanolamine method	109/15	12	56·1/20	0·9600/17	1·4402/17	81·24	95

The triethanolamine method has not yet been fully tested with other aldehydes, but under the optimum conditions for *n*-butaldehyde both propaldehyde and *iso*valeraldehyde gave fair yields of mixtures of the corresponding unsaturated acids rich in the βγ-isomeride. Cinnamaldehyde yielded cinnamylidenemalonic acid, and benzaldehyde either benzylidenemalonic or cinnamic acid, according to the experimental conditions. On the other hand, poor results were obtained with *iso*butaldehyde and heptaldehyde.

It is generally considered that the formation of olefinic acids in this reaction proceeds by way of a primary condensation, followed by the decomposition of an intermediate substituted malonic acid.* The function of the base in the primary condensation has been the subject of controversy. Knoevenagel applied his general hypothesis of the intermediate formation of alkylidene or arylidene bases, which could then react with the malonic acid. Hann and Lapworth (J., 1904, **85**, 46), however, showed that tertiary bases could induce condensations between aldehydes and neutral substances containing a reactive methylene group and contended that it was incorrect to assume a general preliminary condensation between aldehyde and base. They held that the primary function of the base was to facilitate dissociation by lowering the acidity of the medium, and hence that the efficiency of a base should depend mainly on its strength (compare, however, J., 1911, **99**, 2117). Knoevenagel himself had been forced to advance a somewhat similar explanation (G.P. 161171, 1903) to account for the action of tertiary bases, which made it necessary for him to draw a distinction between the modes of action of the two types of base. The more recent suggestions of Rosenmund and Boehm (*Annalen*, 1924, **437**, 125) and of Clemo and Graham (J., 1930, 215) provide no explanation of the activity of tertiary bases.

There seemed to be a possibility that the catalytic action of these tertiary bases in the malonic acid condensation and in the Knoevenagel reaction generally might be due to the presence of traces of secondary base. Hann and Lapworth do not state if their tertiary bases were purified in any way, and the importance of the point led us to repeat the experiments with triethanolamine, using material carefully purified through the crystalline hydrochloride (Knorr, *Ber.*, 1897, **30**, 919), and with pyridine purified through the double zinc chloride (Heap, *J. Amer. Chem. Soc.*, 1921, **43**, 1936). These regenerated bases showed no difference in cata-

---

* It is by no means proved that the postulated intermediates can decompose with the necessary ease under the conditions of reaction; and Verley (*loc. cit.*) has even suggested that unsaturated mono- and di-basic acids are formed by independent processes.

lytic activity from those purified only by distillation. Further, the regenerated triethanolamine effected condensation of the usual Knoevenagel type between *cyclo*pentanone and cyanoacetic acid, although, as in Hann and Lapworth's experiments, the reaction was markedly slower and less complete than that obtained by using, for example, piperidine. It must be concluded, therefore, that tertiary bases as such have a definite catalytic activity.

Hann and Lapworth did not discuss the malonic acid condensation and an extension of their hypothesis to cover this particular reaction would appear to be unjustified. It has been shown that small quantities of weak bases can effect condensation in the presence of a large excess of malonic acid, although the effect of the base in lowering the acidity of the medium must here be negligible. It is not therefore possible to explain the action of bases in these condensations in terms either of the formation of covalent intermediate compounds or of dissociation. In these condensations it is clear that the base will be present mainly as salt and at present it is only possible to draw an analogy between this type of catalytic action and that effected by the salts of bases with mineral acids in the malonic acid condensation and the Knoevenagel reaction generally.

The ease of formation of the $\beta\gamma$-monobasic acids described in this paper suggests the need of further study of the second stage of the reaction. It seems possible that the abnormality of pyridine in excess may be due to a definite difference in the preliminary mode of reaction, whereas the production of $\beta\gamma$-acids by other bases is due to the formation and subsequent decomposition of substituted malonic acids. The present investigation is therefore being extended to a study of the mode of decomposition of the possible intermediates by bases.

The hydrolysis of n-*butylidenemalonic ester* yields an impure acid which on decarboxylation gives almost pure Δ^{β}-*n*-hexenoic acid (p. 750).

EXPERIMENTAL.

Materials.—*n*-Butaldehyde was redistilled, the fraction of b. p. 73—75° being used. The malonic acid was dried over potash in a desiccator. The bases were not specially purified except where mentioned.

Iodometric Analyses.—Ten-minute reactions under the conditions of Linstead and May were used (J., 1927, 2565). The addition varied considerably with the temperature, typical samples of $\beta\gamma$-acid reacting as follows: (1) Iodine addition (J) at 20°, 56·1; at 28°, 69%. (2) $J^{20^{\circ}}$, 54·4; $J^{24\cdot5^{\circ}}$, 61·5%. (3) $J^{23^{\circ}}$, 57·0; $J^{28^{\circ}}$, 63·2%. The mean variation of addition was + 1·5% per degree rise. The data for the reference curve given below for the additions to the pure acids and mixtures at 20° ± 0·25° were determined by Mr. E. G. Noble :

% $\alpha\beta$-Acid	100	90	80	60	40	20	0 ($\beta\gamma$-)
% Iodine addition	0	7·5	15	27	38	48	55·5

The compositions of the various acid mixtures have been determined by correction of the observed additions to 20° and comparison with the reference curve in the usual way.

Condensations of n-*Butaldehyde with Malonic Acid.*—The quantities of reagent used and the procedure followed are described below; deviations from these being given special reference.

(*A*) *A small amount of catalyst being used.* 23 C.c. of *n*-butaldehyde were slowly added with shaking to a mixture of malonic acid (26 g.) and the base (1 c.c.) coöled in ice. The semi-solid mass was left first in ice or at room temperature and then on the water-bath until the evolution of gas had subsided, and was then submitted to steam distillation. The distillate (3 l.) was made alkaline with sodium bicarbonate and the neutral and the basic portion were removed with ether. The alkaline solution was acidified and extracted thoroughly with ether; the extract was dried and the solvent removed.

(*B*) *A large amount of catalyst being used.* The ice-cooled base was treated slowly and with shaking, first with malonic acid (23 g.) and then with *n*-butaldehyde (20 c.c.). Reaction was allowed to proceed at room temperature and on the water-bath. When the evolution of gas was at an end the product was cooled and poured into an excess of 50% sulphuric acid. The liberated acid was then isolated in the same way as from the steam distillate in (*A*).

Pyridine. (*A*) The period of reaction was 1 hour at 0° and 9 hours at 100°. The acid product was a mixture of *n*-hexenoic acids, b. p. 110—112°/11 mm., $d_{4^{\circ}}^{19^{\circ}}$ 0·9625, $n_{D}^{19^{\circ}}$ 1·4432, which remained liquid in a freezing mixture. The process was repeated, pyridine purified through the double zinc chloride (Heap, *loc. cit.*) being used. This was crystallised from absolute alcohol, washed with ether, and decomposed with aqueous caustic soda; the liberated pyridine, after being dried over alkali, had b. p. 114—115°/753 mm. With this pyridine as catalyst, 6 g. of hexenoic acid were obtained with b. p. 103—106°/15 mm., *M* (by titration with baryta) 114·0 (calc., 114·1), $J^{20^{\circ}}$ 42·5%, corresponding to 68% of $\beta\gamma$-acid. This mixture did not solidify in a freezing mixture.

In another experiment with the pure pyridine, after 16 hours at 100°, 27 g. of the aldehyde gave an acid product (9·5 g.), b. p. 115—118°/21 mm., m. p. 0°. After refractionation this had b. p. 113—116°/20 mm., m. p. 0°, $d_{4^{\circ}}^{17^{\circ}}$ 0·9604, $n_{D}^{17^{\circ}}$ 1·4415; $J^{24^{\circ}}$ 51·9, whence $J^{20^{\circ}}$ 46·9%, and $\beta\gamma$-content = 79%.

(B) The condensation in presence of excess of pyridine has been previously used for the preparation of Δ^{α}-n-hexenoic acid by von Auwers and by Goldberg and Linstead (*locc. cit.*). Repeated use of this reaction for preparative purposes has shown that on a 1—2 g.-molecular scale yields of about 80% of hexenoic acid can be obtained by allowing the reaction to proceed for a week at room temperature and for 12 hours or over-night on the water-bath. About a seventh part of this is liquid at room temperature (*ca.* 10% $\beta\gamma$-acid) and the rest is the solid $\alpha\beta$-acid, m. p. 32—33°.

Piperidine. (A) Reaction period : 2 hours at room temperature, 2 days at 100°. Carbon dioxide was evolved only on heating. 60 G. of aldehyde, 88 g. of malonic acid, and 1 c.c. of piperidine yielded 23 g. of n-hexenoic acid, b. p. 104—107°/11 mm., M 114·1, $d_{4^\circ}^{17^\circ}$ 0·9631, $n_{D}^{17^\circ}$ 1·4407, $[R_L]_D$ 31·25, J^{20° 50·2%. On being cooled in ice, the acid solidified to a mass of leaflets melting at 5° alone or when mixed with a sample of Δ^{β}-n-hexenoic acid prepared by equilibration of the $\alpha\beta$-acid by the method of Eccott and Linstead (*loc. cit.*). This acid was further characterised by the preparation of the anilide (m. p. 76°) and p-toluidide (m. p. 95°). These m. p.'s were not depressed when the derivatives were mixed with the original samples of Eccott and Linstead.

In a similar experiment the mixture was kept for 3 days after refluxing and was not distilled in steam. Crystals then slowly separated, which after two crystallisations from ether–light petroleum and one from hydrochloric acid had m. p. 51°. This substance was identified as β-propylglutaric acid by analysis (Found : C, 55·1 ; H, 7·8. Calc. : C, 55·2 ; H, 8·0%), by a mixed m. p. determination, and by the preparation of the anhydride, b.p. 160°/ 12 mm., and semianilide, m. p. and mixed m. p. 127°. Day and Thorpe give m. p. 52°, b. p. 180°/20 mm., and m. p. 128°, respectively, for these compounds (J., 1920, **117**, 1471). 2 G. of this acid were obtained from 18 g. of aldehyde, but the preparation appeared to be fortuitous and could not be repeated.

(B) 16 C.c. of piperidine were used. No gas was evolved during 2 days' standing at room temperature (distinction from pyridine), but carbon dioxide came off freely at 100° (12 hours). On fractionation of the product, 3 g. of acid were obtained, b. p. 121—123°/25 mm., M 114·9 ; J^{18° 41·5%, whence proportion of $\beta\gamma$-acid = 73%. The acid had m. p. 3—4°, and 4° in admixture with the $\beta\gamma$-acid prepared from the $\alpha\beta$-acid.

In another experiment the product was worked up after 3 days' standing at room temperature. The acid fraction was a thick yellow syrup which would not crystallise.

Triethanolamine. Commercial triethanolamine (B.D.H.) was fractionated, the fraction of b. p. 210—220°/12 mm. being used.

(*A*) The reaction mixture containing 0·5 c.c. of this was refluxed for 24 hours at 100°. The product yielded 6 g. of acid, b. p. 104—109°/12 mm., m. p. 5°, *M* 114·2; $J^{20°}$ 54·4%, whence βγ-acid = 98%.

(*B*) *Preparation of pure* Δ^{β}-n-*hexenoic acid.* 60 G. of triethanolamine were used with 26 g. of malonic acid and 23 c.c. of butaldehyde. Successive fractionations of the product gave 13 g., b. p. 104—113°/20 mm., yielding 10·5 g., b. p. 110°/16 mm., *M* 114·0; $n_D^{17°}$ 1·4402, $d_{4°}^{17°}$ 0·9599, whence $[R_L]_D$ 31·24; $J^{20°}$ 56·1%. This acid solidified in ice to masses of white leaflets melting sharply at + 12°; mixtures with the βγ-acid (from equilibration) and with the αβ-acid melted at + 9° and — 13° respectively. The *p*-toluidide melted at 95—96°. This was the purest βγ-acid isolated and was used as the reference substance in subsequent mixed melting-point determinations.

In the preparation of larger quantities of the βγ-acid it was unnecessary to use the full amount of triethanolamine given above. For instance, in one experiment, a mixture of 72 g. of aldehyde, 104 g. of malonic acid, and 120 g. of triethanolamine was left at room temperature for 3 hours and heated on the water-bath overnight. Distillation of the product gave 44 g. of crude βγ-acid and 25 g. of a viscous residue which is still under examination. The crude acid on redistillation boiled almost completely at 96°/9 mm. and melted at 8—12°. For a final purification the solid acid was kept at 10° and small amounts of liquid were poured off from time to time. The solid acid finally melted at 12° and had $J^{20°}$ 55·4%.

In an attempt to isolate intermediate substances the condensation was carried out with an excess of triethanolamine as before but without heating. The acid product was a yellow syrup which changed to an indefinite solid on long standing in a vacuum desiccator. This is being further examined.

Use of purified triethanolamine. The technical material was fractionated, and the fraction boiling above 180° (100 g.) converted into the hydrochloride by Knorr's method (*loc. cit.*). On crystallisation from dilute alcohol, 85 g. of material were obtained, m. p. 177° (Knorr gives 177°). The base isolated from this by Knorr's method was distilled under reduced pressure in a stream of dry hydrogen. Yield: 50 g., b. p. 203—205°/7 mm. With this in small quantity as catalyst, 18 g. of aldehyde yielded 3 g. of acid, b. p. 120°/26 mm., m. p. 9—10°, *M* 114·4, $n_D^{21°}$ 1·4383, $d_{4°}^{21°}$ 0·9596, $J^{25°}$ 61·5% (97% βγ-acid). With an excess of the base as catalyst, the same quantity of aldehyde yielded 10 g. of acid, b. p. 113°/19 mm., m. p. 12°.

Dimethylaniline (A.R.). (*A*) By the usual procedure 4 g. of acid were obtained, b. p. 113—119°/20 mm., m. p. 7—8°, *M* 114·4; J^{25° 60·0%, whence βγ-acid = 92%.

(*B*) When 60 g. of the base were used, gas was not evolved at room temperature (2 days) but rapidly at 100° (3 hours). 6·5 G. of acid were obtained, b. p. 113—119°/20 mm., m. p. 10°, *M* 114·6, $n_D^{23^\circ}$ 1·4398, $d_{4^\circ}^{23^\circ}$ 0·9615, J^{24° 62·1% (100% βγ-acid).

Diphenylamine. (*A*) 0·5 C.c. of the recrystallised base, dissolved in 10 c.c. of ether, was used. On distillation of the acid product a fraction (3 g.) was obtained, b. p. 117—121°/23 mm., m. p. 7°, *M* 115·0, $n_D^{20^\circ}$ 1·4410, $d_{4^\circ}^{20^\circ}$ 0·9628, J^{24° 57% (βγ-acid = 88%).

The use of an excess of this base led to resinification.

Quinoline. (*A*) 1 C.c. of the freshly distilled base was used, the mixture being left at room temperature for 1 hour and on the water-bath for 20 hours. The acid product (3 g.) had b. p. 112—117°/17 mm., m. p. 3°, *M* 112·0, J^{25° 49·9% (equivalent to 68% of βγ-acid).

(*B*) 50 G. of the freshly distilled base being used, no gas was evolved from the reaction mixture in 2 days at room temperature (contrast pyridine), but evolution was complete after 4 hours' heating on the water-bath. Redistillation of the acid product yielded material, b. p. 112—115°/18 mm., m. p. 6—7°, *M* 113·6, $n_D^{20^\circ}$ 1·4377, $d_{4^\circ}^{20^\circ}$ 0·9651, J^{25° 55·7% (βγ-acid = 80%).

Aniline. (*A*) 24 Hours' refluxing on the steam-bath yielded an impure acid (3 g.), b. p. 110—118°/12 mm., m. p. 1—2°, *M* 120, the quality of which was not improved by refractionation.

(*B*) No hexenoic acid could be isolated.

Ammonium chloride. (*A*) 1 G. of the salt was used, and the mixture heated at 100° for 20 hours. The acid product boiled indefinitely, but on redistillation of the fraction of b. p. 115—130°/22 mm. (m. p. 3—4°), 4 g. of acid were obtained having b. p. 114—118°/15 mm., *M* 113·4, $n_D^{23^\circ}$ 1·4419, $d_{4^\circ}^{23^\circ}$ 0·0706, J^{20° 43·2% (70% of βγ-acid). The acid melted at 4—5°, and at 7—8° in admixture with an equal quantity of the pure βγ-acid (m. p. 12°).

Aniline hydrochloride. (*A*) 1 G. of the salt was used, and heating on the water-bath continued for 5 hours. The acid boiled indefinitely, but a fraction (4 g.) was ultimately obtained, b. p. 109—118°/15 mm., *M* 113·5, $n_D^{25^\circ}$ 1·4378, $d_{4^\circ}^{25^\circ}$ 0·9614, J^{24° 59·2% (94% of βγ-acid). The m. p., 7°, was raised to 9° on admixture with an equal part of the pure βγ-acid.

Attempted Preparation of Butylidenemalonic Acid.—Ethyl n-*butylidenemalonate*, $CH_2Et{\cdot}CH{:}C(CO_2Et)_2$, was prepared by a method similar to that used by Schryver (J., 1893, **63**, 1344) for the corresponding *iso*butylidene compound. A mixture of freshly distilled *n*-butaldehyde (72 g.), ethyl malonate (80 g.), and acetic anhydride (76 g.) was heated in pressure bottles at 100° for 24 hours. The liquid was distilled up to 150° under atmospheric pressure and then under reduced pressure; 80 g. of the crude ester were then obtained, b. p. 128—160°/23 mm. On exhaustive fractionation this yielded 44 g. boiling from 143—146°/25 mm. (b. p., 144°/25 mm.) with $n_D^{19\cdot5°}$ 1·4434, $d_{4°}^{19\cdot5°}$ 1·0029, whence $[R_L]_D = 56\cdot64$ (Found: C, 61·5; H, 8·4. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·4%).

The ester (50 g.) was treated with a solution of 27 g. of caustic potash in 240 c.c. of water and 200 c.c. of alcohol. The acid, isolated in the usual way on completion of the hydrolysis, was left over paraffin wax in a vacuum desiccator. The viscous yellow liquid obtained (30 g.) failed to solidify during several months. It was completely soluble in aqueous sodium bicarbonate and the solution immediately decolorised permanganate. The high equivalent (Found: 143) indicated the presence of monobasic or polymeric impurities.

When heated at 160° for 2 hours, the acid evolved carbon dioxide vigorously. On distillation of the residue, a fraction, b. p. 110—130°/15 mm., was obtained in poor yield. This was freed from lactone in the usual way, 1 g. of acid being obtained, b. p. 108—111°/14 mm., $n_D^{20°}$ 1·4374, $d_{4°}^{20°}$ 0·9594, whence $[R_L]_D$ 31·12. The acid solidified to the characteristic white leaflets of the βγ-acid and melted at 5°. A mixture with the αβ-acid failed to solidify in a freezing mixture. The acid was further identified by the preparation of the βγ-*p*-toluidide, m. p. and mixed m. p. 95—96°.

Other Condensations using Triethanolamine.—(1) Propaldehyde (18 c.c.), malonic acid (26 g.), and triethanolamine (0·5 c.c.), condensed under conditions (*A*), yielded an acid fraction, b. p. 100—110°/27 mm., which on redistillation gave 2 g. of *n*-pentenoic acid, mainly the βγ-acid, b. p. 104—105°/27 mm., *M* 101 (calc., 100), $J^{18°}$ 33·1%.

(2) Under conditions (*B*), 28 c.c. of propaldehyde, 39 g. of malonic acid, and 50 g. of the base yielded 7 g. of *n*-pentenoic acid, b. p. 103—104°/24 mm., *M* 101, $J^{18°}$ 34·8%.

(3) With *iso*butaldehyde and with heptaldehyde both sets of conditions gave very incomplete condensation and the acid product was of poor quality.

(4) *iso*Valeraldehyde also gave poor material under conditions (*A*), but when an excess of the base was used, 26 c.c. of the aldehyde yielded 6 g. of (mainly Δ^{β}-) *iso*heptenoic acid, b. p. 119—122°/19 mm., *M* 127 (calc., 128), $J^{18°}$ 41·5%.

(5) Cinnamaldehyde (35 g.), malonic acid (26 g.), and triethanolamine (0·5 c.c.) were heated together on the water-bath for 7 hours,

the mixture solidifying after 2 hours. The yellow mass was extracted with bicarbonate solution and from this extract cinnamylidenemalonic acid was obtained as a yellow crystalline solid (6 g.), m. p. 208° after two crystallisations from dilute alcohol (compare Riiber, *Ber.*, 1904, **37**, 3123).

(6) Benzaldehyde (5·1 g.), malonic acid (5·2 g.), and triethanolamine (0·7 g.) were heated together at 100° for 18 hours. The acid product insoluble in water was cinnamic acid (1·3 g., m. p. 133°). In another experiment, in which the mixture was not heated, benzylidenemalonic acid (1·0 g.) was formed, m. p. 196° [Found : M (dibasic), 96·4. Calc., 97·0].

(7) A mixture of *cyclo*pentanone (4·2 g.), cyanoacetic ester (5·6 g.), and triethanolamine (1·5 g., purified through the hydrochloride) was left at room temperature for 10 days. Water had then separated and the mixture was semi-solid. The mixture was cooled in ice and submitted to rapid filtration. The solid (2·1 g. after being drained on a porous tile) was almost pure *cyclo*pentylidenecyanoacetic ester, m. p. (without crystallisation) and mixed m. p. 54° (compare Harding and Haworth, J., 1910, **97**, 486). The mother-liquor slowly deposited crystals of the same substance (3·4 g.; 40% yield in all). In another experiment, in which an equimolecular amount of the pure base was used, the same yield (40%) of the solid cyano-ester was obtained.

The authors are indebted to the Government Grant Committee of the Royal Society and to the Chemical Society for grants which have defrayed much of the cost of this work.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7.

[*Received, February* 11*th*, 1931.]