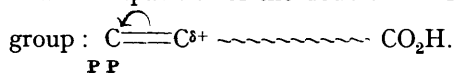


**142.** *Investigations of the Olefinic Acids. Part VII. The Preparation of  $\Delta^{\beta}$ -Acids.*

By R. P. LINSTEAD, E. G. NOBLE, and (in part) E. J. BOORMAN.

RECENT interpretations of such processes as tautomeric change and the additive reactions of olefins on an electrochemical basis assume that the ethylenic double bond is capable of polarising at demand. The present group of papers (Parts VII to XI) provides, it is believed, an independent proof of this capacity and illustrates both the influence of alkyl groups in determining the direction of this polarisation and its result in additive reactions.

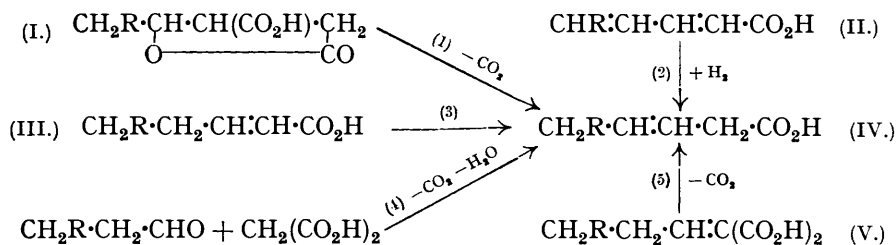
The proof of the polarisability of the double bond is provided by a series of measurements of an *electrical* quantity, namely, the conductivity of unsaturated acids (Part VIII); and a comparison between the dissociation constants of a series of such acids indicates the relative capacities of the double bonds for anionoid polarisation away from the carboxyl



The obvious assumption is next made that the acids with a high capacity for this process of adjustment are those in which the *normal preferred* direction of polarisation of the double bond (*i.e.*, that operative in reactions in which it behaves purely as if in an olefin) is more in this direction than it is in acids with a lower capacity for such adjustment. It then becomes possible to anticipate the orientation of the addition of molecules of the type of hydrogen bromide to the various acids; for those containing a double bond which normally polarises away from the carboxyl group will be those tending under suitable conditions to add the negative end of the addendum towards this group, and vice versa.

Parts IX, X, and XI illustrate the orientation of heterogeneous addition to the acids; and the present paper is concerned with some necessary preliminary preparative work.

The principal methods which have been used for the preparation of  $\Delta^\beta$ -olefinic acids are exemplified in the following scheme: (1) Fittig, *Annalen*, 1889, **255**, 1; (2) *idem, ibid.*, 1872, **161**, 309; 1880, **200**, 21; (3) Eccott and Linstead, *J.*, 1929, 2153; (4) Boxer and Linstead, *J.*, 1931, 740; (5) Riiber, *Ber.*, 1905, **38**, 2743; Kon and Speight, *J.*, 1926, 2727.



The comparative value of the methods for the preparation of  $\Delta^\beta$ -olefinic acids with unbranched chains has now been examined, and it may be presumed that the results are applicable to acids substituted by alkyl at the  $\delta$ -carbon or beyond. For this purpose, the preparation of  $\Delta^\beta$ -*n*-hexenoic, -pentenoic, and -butenoic acids has been studied.

$\Delta^\beta$ -*n*-Hexenoic Acid (IV, R = Me).—Eccott and Linstead and Boxer and Linstead (*loc. cit.*) have shown that methods (2) and (5) are unsatisfactory for the synthesis of this substance, and (3) and particularly (4) give better results. Using method 1, Fittig and Delisle (*Annalen*, 1889, **255**, 56) obtained an acid, liquid at  $-18^\circ$ , which gave a *p*-toluidide, m. p.  $95.5^\circ$  (Fichter and Pfister, *Ber.*, 1904, **37**, 1997). We, by the same method, have obtained an acid, m. p.  $-0.5^\circ$  to  $+2.5^\circ$ , which has a low iodine addition (46%) and therefore contains 20—25% of the  $\Delta^\alpha$ -isomeride.

The triethanolamine method (4) for the preparation of the acid from malonic acid and *n*-butaldehyde has in our hands given reproducible yields of over 40% of an acid of constant properties; there is no appreciable formation of an isomeric acid and "purification" of the solid acid by partial esterification leaves its properties unchanged. The principal sources of loss arise from the auto-condensation of the aldehyde, and from its condensation with two molecules of malonic acid to yield  $\beta$ -*n*-propylglutaric acid. Possibly the formation of this glutaric acid proceeds by an addition of malonic acid to  $\Delta^\alpha$ -unsaturated material, which would account for the remarkable absence of the latter from the unsaturated products of the reaction.

$\Delta^\beta$ -*n*-Pentenoic Acid (IV, R = H).—The methods of Fittig and co-workers (*Annalen*, 1889, **255**, 27; 1894, **283**, 66, 83) give mixtures, but almost pure  $\Delta^\beta$ -acid was prepared by Goldberg and Linstead (*J.*, 1928, 2343) and Burton and Ingold (*J.*, 1929, 2022) by a modification of Thiele and Jehl's method (*Ber.*, 1902, **35**, 2320). In none of these cases was the acid obtained in a solid form.

The triethanolamine method of Boxer and Linstead (*loc. cit.*) has now been developed to yield pure  $\Delta^\beta$ -*n*-pentenoic acid, m. p.  $+1^\circ$ , in about 35% yield. The acid prepared from the crystalline dibromide by Burton and Ingold's method is almost identical with this and melts at  $+0.5^\circ$ . As with the higher homologue, the reaction between propaldehyde and malonic acid in the presence of triethanolamine gives rise to some 30% of the corresponding glutaric acid.

$\Delta^{\beta}$ -*n*-Butenoic Acid,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ .—This acid can only be prepared in poor yield and doubtful purity by the general methods already mentioned. Application of the triethanolamine method to acetaldehyde gave a very poor yield of an acid of the correct properties, together with the corresponding glutaric acid. Houben's method (*Ber.*, 1903, **36**, 2897) also gave a poor yield, but the product yielded the correct dibromide and was nearly pure (m. p.  $-42^\circ$ ). A pure acid is easily obtained by the method of Bruylants (*Bull. Soc. chim. Belg.*, 1922, **31**, 228; 1924, **33**, 334). A considerable number of preparations gave a product of remarkably concordant physical properties, which melted sharply at  $-35^\circ$ , and yielded a dibromide identical with that prepared by the method of Houben.

Contrary to expectation, vinylacetic acid, although easily isomerised, is not an exceptionally unstable substance when kept at room temperature in the pure state.

## EXPERIMENTAL.

Iodine additions (*J*) were determined at  $20^\circ$  for 10 min. Recorded m. p.'s are corrected for stem exposure.

$\Delta^{\beta}$ -*n*-Hexenoic Acid.—(a) *Triethanolamine method*. To a cooled mixture of freshly distilled *n*-butaldehyde and triethanolamine (1 g.-mol. of each), dry malonic acid (1 g.-mol.) was added, and the whole shaken until homogeneous (slight cooling being necessary at first) and then, after 2 days, heated on the steam-bath till evolution of gas had ceased (over-night). The liquid was cooled and acidified with 50%  $\text{H}_2\text{SO}_4$  (by wt.); the upper layer of olefinic acid was separated, the aq. layer extracted four times with  $\text{Et}_2\text{O}$ , the combined acid and extracts washed with  $\text{H}_2\text{O}$ , the solvent removed, and the residue extracted with dil.  $\text{Na}_2\text{CO}_3$  aq., in which the last trace of acid dissolves very slowly. The alkaline solution was extracted four times with  $\text{Et}_2\text{O}$  to remove aldehydic polymerides, and acidified, and the acid was extracted as before, washed, dried, recovered, and distilled, giving a fraction, b. p.  $110\text{--}120^\circ/20$  mm., which contained the hexenoic acid, and a high-boiling residue (see below). On redistillation the hexenoic acid fraction boiled almost entirely at  $110^\circ/15$  mm. (yield, 40—42%; occasionally 52%). It was further purified by freezing it at  $0^\circ$  and allowing it to warm slowly, the small amount of material melting below  $12^\circ$  being rejected. The solid acid was then unchanged in properties after partial esterification and hydrolysis of the ester (Sudborough and Thomas, *J.*, 1911, **99**, 2307; Eccott and Linstead, *loc. cit.*), as is shown by the following figures :

	B. p./15 mm.	M. p.	$n_D^{20}$ .	$d_4^{20}$ .	<i>J</i> .
Acid purified by fractional melting .....	110°	12°	1.4391	0.9630	55.8
„ „ partial esterification ...	111	11.5	1.4390	0.9635	55.4

The high-boiling residue mentioned above was distilled (260 g.) under reduced press. Decomp. and liberation of  $\text{CO}_2$  occurred, and on redistillation two main fractions, b. p.  $185\text{--}190^\circ/23$  mm. (55 g.) and  $190\text{--}200^\circ/23$  mm. (80 g.), were obtained. The first of these was mainly  $\beta$ -*n*-propylglutaric anhydride; on treatment with aniline in  $\text{C}_6\text{H}_6$  it yielded the half-anilide, m. p.  $125\text{--}126^\circ$  (see below). The second fraction, most of which boiled at  $198\text{--}199^\circ/23$  mm., was largely the corresponding free acid. It was converted by  $\text{AcCl}$  into the anhydride, which after purification was converted (1) into  $\beta$ -*n*-propylglutaric acid, m. p.  $51^\circ$ , equiv. 87.4 (calc., 87.1) after crystallising twice from  $\text{Et}_2\text{O}$ —light petroleum and once from dil.  $\text{HCl}$ , and (2) into the half-anilide, m. p.  $127^\circ$  after two crystns. from  $\text{C}_6\text{H}_6$ . Day and Thorpe (*J.*, 1920, **117**, 1471) give acid, m. p.  $52^\circ$ ; half-anilide, m. p.  $128^\circ$ ; anhydride, b. p.  $180^\circ/20$  mm. The m. p.'s of our solid derivatives were not depressed by admixture with the corresponding authentic samples.

(b) *From ethylparaconic acid*. The acid (m. p.  $82^\circ$ ) was prepared by the method of Fittig and Delisle (*loc. cit.*) as modified by Fichter and Probst (*Annalen*, 1910, **372**, 76). The yield was poor—5 g. from 1 g.-mol. of anhyd. sodium succinate. The acid was decarboxylated by the method used by Goldberg and Linstead for terebic acid (*loc. cit.*), the unsaturated acid being purified by distillation in steam and extraction through  $\text{NaHCO}_3$ . The product (1.0 g.) boiled at  $98^\circ/6$  mm. and solidified at  $-15^\circ$  to a cryst. mass of m. p.  $-1^\circ$  to  $+2^\circ$ , mixed m. p. with the pure acid,  $+1^\circ$  to  $+2.5^\circ$  (Found: equiv. 114.2; calc., 114.1; *J*, 46%).

[With E. J. BOORMAN.]

$\Delta^{\beta}$ -*n*-Pentenoic Acid.—Preliminary expts. on the condensation of propaldehyde and malonic acid by means of bases in various amounts gave the following results :

Base.	Amount.	Pentenoic acid (equiv. 100·1).			
		Yield.	B. p./20 mm.	Equiv.	J.
Triethanolamine	molecular	20	98°	100	38
Dimethylaniline	"	23	96	98·7	37·5
Pyridine	trace	15	95	98·2	33
Piperidine	"	14	94	98·5	36·5

As pure  $\Delta^\beta$ -pentenoic acid has an iodine addition of 38·5% and that to the  $\Delta^\alpha$ -acid is negligible, it will be seen that all the bases produce mainly  $\Delta^\beta$ -acid (cf. butaldehyde; Boxer and Linstead, *loc. cit.*).

On account of the comparatively objectionable nature of dimethylaniline, triethanolamine was selected for further work. The best yields (32—36%) were obtained by the addition of the malonic acid to a mixture of the base and aldehyde with vigorous shaking.  $\Delta^\beta$ -*n*-Pentenoic acid was isolated from the product and purified by the methods already described for the higher homologue. It formed flattened needles, m. p. 1°; b. p. 90°/10 mm.;  $d_4^{20}$  0·9850;  $n_D^{20}$  1·4348; whence  $[R_L]_D$  26·51 (calc., 26·36); J, 38·5% (Found: C, 60·1; H, 8·0; equiv., 100·3. Calc. for  $C_5H_8O_2$ : C, 60·0; H, 8·1%; equiv., 100·1). These physical properties are close to those recorded by v. Auwers for the reduction product of vinylacrylic acid (*Annalen*, 1923, 432, 46).

The thick brown oil remaining after the first distillation of the pentenoic acid distilled with partial decarboxylation, some 50% boiling at about 182°/22 mm. This distillate became almost completely solid in 3 months, and was then drained and recrystallised from  $C_6H_6$  and light petroleum. It was identified as  $\beta$ -ethylglutaric acid by its m. p. (74°; lit., 74°), equiv. (80·4; calc., 80·0), and by a mixed m. p. determination with an authentic sample.

The  $\Delta^\beta$ -pentenoic acid described above had an iodine addition considerably less than that recorded by Goldberg and Linstead (46·8%) for a sample prepared by the reduction of vinylacrylic acid. On this account its purity was checked by its conversion into the cryst. dibromide, m. p. 64° (cf. Fittig and Mackenzie, *loc. cit.*), and regeneration (Burton and Ingold, *loc. cit.*). The recovered material (70%) and the original had almost identical properties: m. p. + 0·5°; b. p. 95°/17 mm.;  $n_D^{20}$  1·4354;  $d_4^{20}$  0·9852; equiv. 101·2; J, 38·9%; and it is clear that both these methods give pure material. The difference between the iodometric figures mentioned above is to be attributed mainly to the presence of a trace of the highly additive vinylacrylic acid in the old material.

$\Delta^\beta$ -*n*-Butenoic (Vinylacetic) Acid.—(a) The triethanolamine method gave an optimum yield from 26 g. of malonic acid and an excess of MeCHO of 1 g. of a liquid acid, b. p. 70°/12 mm., and 1 g. of a high-boiling residue which solidified on long standing and was shown to be  $\beta$ -methylglutaric acid, m. p. 86° (after two recrystns. from  $C_6H_6$ -light petroleum), mixed m. p. with authentic sample, 86°; equiv. 73·2 (calc., 73·1).

(b) Following Houben (*loc. cit.*), 50 g. of allyl bromide gave 1 g. of vinylacetic acid, b. p. 72—73°/15 mm., m. p. — 42°, which yielded the dibromide, m. p. 49—50°, of Fichter and Sonneborn (*Ber.*, 1902, 35, 938). Vigorous mechanical stirring did not improve the yield.

(c) Using essentially the method of Bruylants (*loc. cit.*), we obtained the best yields by the following procedure: 30 G. (not more) of allyl cyanide (Breckpot, *Bull. Soc. chim. Belg.*, 1930, 39, 465) were cooled in ice, and 25 c.c. of conc.  $H_2SO_4$  added slowly in small quantities, the mixture being cooled after each addition, particularly at first, and kept below 40° throughout. Any excessive local overheating led to an uncontrollable reaction and much carbonisation. Too much cooling, on the other hand, stopped the reaction. The mixture was finally kept until all smell of the nitrile had disappeared and a glassy mass remained (4—5 days). A weight of  $H_2O$  equal to that of the  $H_2SO_4$  used was then added, and the mixture heated rapidly on the steam-bath with frequent shaking until a reaction set in and the mass had dissolved with the formation of two layers (about 30 min.). The mixture was cooled, and the vinylacetic acid isolated by means of  $Et_2O$  in the usual way, dried, and distilled. About 12 g. of a fraction, b. p. 70—72°/13 mm., were obtained and this on two refractionations in vac. with a column yielded pure vinylacetic acid (equiv., 86·1; calc., 86·1). Six different preps. gave material with the following physical properties:

Prepn.	M. p.	B. p.	$n_D^{20}$ .	$d_4^{20}$ .	Prepn.	M. p.	B. p.	$n_D^{20}$ .	$d_4^{20}$ .
1	—35°	72°/14 mm.	1·4220	1·0096	4	—35°	70·5°/12 mm.	1·4222	1·0093
2	—35	78/21	1·4220	1·0095	5	—35	69/10	1·4222	1·0091
3	—35·5	71/12	1·4221	1·0098	6	—35	69/10	1·4220	1·0090

Whence  $[R_L]_D = 21·66$ ; calc., 21·74.

The agreement between these figures leaves no doubt that the substance is homogeneous. The m. p. is a little higher than that recorded by Bruylants ( $-38^{\circ}$ ) and by Lespieau ( $-39^{\circ}$ ; *Bull. Soc. chim.*, 1905, 33, 63), the density is almost identical with that given by Bruylants, and the refractive index corresponds with that ( $1.4257_D$  at  $15^{\circ}$ ) given by Fichter and Sonneborn (*loc. cit.*).

The acid prepared from allyl cyanide yielded a dibromide, m. p.  $50^{\circ}$ , which did not depress the m. p. of the dibromide of the Houben product.

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