152. *The Preparation and Estimation of Nitriles of* Δ^{α}- *and* Δ^{β}-*Olefinic Acids.*

By R. A. Letch and R. P. Linstead.

Bruylants (*Bull. Soc. chim. Belg.*, 1932, **41**, 309) has questioned the purity of some of the olefinic nitriles investigated by us (J., 1932, 443) : the points at issue may be dealt with under the headings used by him.

(1) The Belgian school have employed the bromometric method of Heim (*Bull. Soc. chim. Belg.*, 1930, **39**, 458) for the estimation of Δ^{β}-nitriles. In our previous work, we applied this method satisfactorily to Δ^{β}-*n*-butenonitrile, but found that higher homologues such as Δ^{β}-*n*- and -*iso*-hexenonitriles gave variable and incomplete addition. To account

for the difference Bruylants suggests that Heim's conditions could not have been exactly followed by us and that, as our preparation of Δ^{β}-*iso*hexenonitrile gave a mean bromine addition of about 65%, it must have been contaminated with the non-additive Δ^{α}-isomeride. In support of this, Baerts (*Bull. Soc. chim. Belg.*, 1932, **41**, 314) has obtained a bromine addition of 98·8% to the Δ^{β}-nitrile.

We have repeated the preparation of this Δ^{β}-nitrile by decarboxylating the corresponding α-cyano-acid and find that the velocity of the addition of bromine to it is dependent on the conditions of mixing and shaking the solutions. In the period specified by Heim (12 seconds) the values obtained were variable and well below 100%, but after 3 minutes' shaking a reproducible maximum corresponding to 99·7% addition was obtained. The Δ^{β}-nitrile prepared by our method is therefore free from the Δ^{α}-isomeride.

α-Δ^{1}-*cyclo*Hexenylbutyronitrile, prepared by dehydrating the corresponding amide (Kandiah and Linstead, J., 1929, 2139), gave an addition of 50—60% in 12 seconds, which reached a steady maximum of 99% only in 10 minutes. Heim's method can therefore only be generally applied to the estimation of unsaturated nitriles when a period of reaction is allowed sufficient to give a constant value for the addition to the Δ^{β}-isomeride.

(2) In the light of these and previous results, it is not possible to accept Bruylants' criticism of our preparative methods and it seems clear that (i) the dehydration of pure unsaturated amides yields the corresponding nitriles and (ii) that, as von Auwers (*Ber.*, 1923, **56**, 1172) and others have stated, the decarboxylation of Δ^{α}-cyano-acids normally yields the corresponding Δ^{β}-nitriles. The amount of isomeric impurity formed in these reactions is generally so small that it is easily removed by fractionation; for example, the Δ^{β}-*iso*hexenonitrile mentioned above gave the theoretical bromine addition after only two fractionations. It does not appear, however, that this is always the case for Δ^{β}-nitriles prepared by decarboxylation; *e.g.*, α-cyano-Δ^{α}-pentenoic acid gives a mixture containing a little Δ^{α}-nitrile (Fonteyn; quoted by Bruylants), and α-cyano-Δ^{α}-butenoic acid gives exclusively the Δ^{α}-nitrile (Letch and Linstead).

(3) We did not attempt in our previous paper to assess the purity of Bruylants and Minetti's *trans*-Δ^{α}-*iso*hexenonitrile and there is no implication that this was impure.*

(4) Bruylants and Ernould's preparation of Δ^{α}-*n*-hexenonitrile (*Bull. Acad. roy. Belg.*, 1931, **17**, 1174), which was described after the completion of our work, gave a product closely resembling that prepared by dehydrating Δ^{α}-hexenoamide. Our preparation of this nitrile gave no addition of bromine under Heim's conditions, and may therefore be taken as being free from the Δ^{β}-isomeride.

The results obtained in the study of the tautomeric changes of these substances which were described in our previous paper remain unaffected. The fact that Baerts (*loc. cit.*) was able to isolate pure Δ^{β}-*iso*hexenonitrile after a large number of distillations at atmospheric pressure confirms our view that these nitriles, unlike the parent acids, are not isomerised at their boiling points.

This paper has been communicated privately to Professor Bruylants and he is now in general agreement with our interpretation of the results.

EXPERIMENTAL.

Δ^{β}-*iso*Hexenonitrile (1) and α-Δ^{1}-*cyclo*hexenylbutyronitrile (2) were freshly prepared. The Δ^{α}- and Δ^{β}-*n*-hexenonitriles (3 and 4 respectively) were old preparations. The last of these appears to be slightly contaminated with the Δ^{α}-isomeride. After two fractionations these had the following properties :

Nitrile.	B. p.	$n_D^{20°}$.	$d_{4°}^{20°}$.	$[R_L]_D$.
1	62°/20 mm.	1·4350	0·8510	29·20
2	112/12	1·4750	0·9216	45·50
3	60/17	1·4380	0·8272	30·15
4	62/20	1·4299	0·8410	29·20

---

[*] Attention may be drawn to some misprints in Bruylants' last paper. On p. 310, the molecular refractivity of this Δ^{α}-nitrile is given as 29·26, for observations by both schools, and the density, observed by Bruylants and Minetti, as 0·8231. Our published value for $[R_L]_D$ is, however, 30·24 (exaltation, 0·98) and the figures actually given by Bruylants and Minetti are 30·156 and 0·82131 respectively.

The following mean additions were obtained by Heim's method, the bromine solution being added from a pipette :

Time of reaction	12 secs.	30 secs.	1 min.	2 mins.	3 mins.	4 mins.	5 mins.	10 mins.
% Addition to 1	93*	—	96·6	98·5	99·7	99·8	—	99·6
,, ,, 2	(50—60)	—	84·5	91·7	94·3	—	96·7	98·7
,, ,, 3	0	—	—	1·8	—	—	2·5	3·8
,, ,, 4	(69—76)	89·9	91·5	94·6	95·2	95·0	—	—

* Or 70—75% if the bromine solution was run in from a fast-running burette.

We are indebted to the Chemical Society for a grant (to R. A. L.).

IMPERIAL COLLEGE, LONDON, S.W. 7.

[*Received, April 7th,* 1933.]