309. *The Hydration of Acetylenes. Part I. $\Delta^{9:10}$-Undecynoic Acid (Undecolic Acid).*

By (Miss) M. L. Sherrill and J. C. Smith.

Although much information is available on the hydration of acetylene to acetaldehyde with sulphuric acid or acetic acid in presence of mercuric salts, the hydration of other acetylenes has not been so carefully studied.

The object of the present research has been to find the proportions of the isomeric keto-acids produced by hydration of $\Delta^{9:10}$-undecynoic acid, $CH_3{\cdot}C{\vdots}C{\cdot}[CH_2]_7{\cdot}CO_2H$. Owing to the greater repulsion of electrons from the polymethylene chain than from the methyl group (general effect), the carbon atom C_{10} will have a negative charge more frequently than will C_9, *i.e.*, $CH_3{\cdot}\overset{-}{C}{\vdots}\overset{+}{C}{\cdot}$, which should lead to a higher proportion of 9-keto-acid in the hydration product. This is found to be true for hydration with sulphuric acid (59% 9-keto-acid and 41% 10-keto acid), but with mercuric acetate in acetic acid the product is 46% of 9-keto- and 54% of 10-keto-acid. Apparently an electromeric rearrangement is induced by the mercuric salt.

Addition of hydrogen bromide to $\Delta^{9:10}$-undecenoic acid yielded 50% each of 9- and 10-bromoundecoic acids (Abraham, Mowat, and Smith, this vol., p. 948) so that such different alkyl groups as CH_3 and $[CH_2]_7{\cdot}CO_2H$ did not produce sufficient difference of polarity in the double bond to cause any appreciable orientation of the addition product.

It would be of interest to examine the addition products of hydrogen bromide and the corresponding acetylenic acid ($\Delta^{9:10}$-undecynoic acid) but the difficulties of a quantitative investigation appear serious, and in the meantime a study of the hydration products has been undertaken.

Hydration with sulphuric acid gave 59% of 9-keto- and 41% of 10-keto-undecoic acid, and hydration with mercuric acetate gave 46% of 9-keto- and 54% of 10-keto-acid (compare

Myddleton and Barrett, *J. Amer. Chem. Soc.*, 1927, **49**, 2258). Such a difference between the products of these two methods was unexpected and appeared not to have been observed previously; but the results by each method were very consistent under a variety of conditions, and the difference was not due to loss of one of the isomerides in isolation of the products. As the "general effect" of the alkyl groups should be to make C_{10} more negative than C_9 $(\mathrm{CH_3}{\cdot}\overleftarrow{\underset{-}{\mathrm{C}}{\vdots}\underset{+}{\mathrm{C}}{\cdot}[\mathrm{CH_2}]_7}{\cdot}\mathrm{CO_2H})$, hydration should produce an excess of 9-keto-acid, and therefore it is the reaction with mercuric acetate in acetic acid which gives the anomalous result. Since the proportion of the isomerides was the same at 40° as at 90°, the effect could not be attributed to temperature, and either the solvent or the mercury salt must be responsible. An experiment in which a mixture of sulphuric acid (4 mols.) and acetic acid (5 mols.) was used for hydration gave the same result as sulphuric acid alone, so the acetic acid appeared to exert no influence, and the anomalous result must be attributed to mercuric acetate. It was not possible to test the effect of mercuric salts on the hydration in presence of sulphuric acid because of the sparing solubility of mercuric sulphate in sulphuric acid of sufficient concentration to dissolve the undecynoic acid.

It is possible for an initial complex formed from the undecynoic acid and the mercuric acetate to undergo at least three changes : it may (i) decompose, regenerating the components, (ii) react immediately to form either 9- or 10-keto-acid derivatives depending on the original orientation of the complex, or (iii) undergo a rearrangement and then react to form the keto-acid derivative differing from that indicated by the original orientation. The simplest rearrangement would be that in which the mercuric acetate part of the complex induced the change $\mathrm{CH_3}{\cdot}\overset{-}{\mathrm{C}}{\vdots}\overset{+}{\mathrm{C}}{\cdot}$ to $\mathrm{CH_3}{\cdot}\overset{+}{\mathrm{C}}{\vdots}\overset{-}{\mathrm{C}}{\cdot}$.

EXPERIMENTAL.

9-Ketoundecoic acid (Abraham, Mowat, and Smith, *loc. cit.*) was crystallised from benzene–light petroleum to constant m. p. 59·0° (thermometer in the liquid) and 57—59·5° (capillary tube). An unstable transparent form melted at 57·2°. 10-Ketoundecoic acid, similarly purified, had m. p.'s 60·2° and 58—60·5° respectively under the same conditions. The unstable form had m. p. 58·45°.

Mixtures of 9- *and* 10-*Ketoundecoic Acids.*—These all crystallised readily, and on the 9-keto-acid branch of the curve the m. p.'s (clearing points) were sharp and unambiguous, only one form of crystal being present. On the 10-keto-acid branch, a bulky mass of crystals melted sharply, leaving a varying amount of fine crystals which in turn cleared sharply. Near the eutectic a third and flocculent type of crystal mass was usually obtained instead of the lowest-melting form. On melting, this left a small residue of the fine, high-melting crystals. Although the conditions governing the formation of each type of crystal were not elucidated, the distinct differences in appearance told immediately which form was being observed, and there was little difficulty in using this branch of the curve for analysis. In consequence of the polymorphism the eutectic m. p. was indefinite but a prolonged halt at 42·4° was observed. For all temperatures below 54° a thermometer was used which involved a slight correction for emergent stem; this correction was not applied, but the same thermometer was used for the m. p.'s of the synthetic mixtures and those of the reaction products.

9-Keto-acid, mols. % ..	100	96·8	91·4	85·1	71·9	63·8	58·3	57·0	55·0	53·6	53·1	51·1
M. p. (I)	59·0°	58·05°	56·6°	54·8°	51·1°	48·3°	46·3°	45·7°	45·0°	44·35°	44·2°	43·1°

9-Keto-acid, mols. %	50·0	48·0	46·8	45·3	40·15	30·2	19·8	9·8	0·0
M. p. (I)	43·35°	44·3°	45·25°	46·4°	48·3°	51·8°	54·9°	57·65°	60·2°
,, (II)	—	—	—	45·65°	47·6°	—	—	—	—
,, (III)	42·25°	42·9° (?)	—	—	46·15°	49·7°	53·0°	55·9°	58·45°

$\Delta^{9:10}$-*Undecynoic Acid* (Harris and Smith, J., 1935, 1108).—The crude acid (b. p. 132°/0·1 mm., m. p. 56—58°) was crystallised from benzene–light petroleum to constant m. p. 59·9° (thermometer in the liquid), 60—61° (capillary tube).

Hydration of Undecynoic Acid with Sulphuric Acid.—General procedure. Powdered undecynoic acid (5 g.) was gradually added to sulphuric acid (40 c.c., 80—90%) stirred at 5—8°. The resulting solution was kept for ½ hour at 5° and then left for several hours at room temperature;

it gradually darkened. After the mixture had been poured on ice (100—200 g.), extraction with ether gave approximately 5 g. of residue which, distilled at 152—156°/0·1 mm., yielded approx. 4·6 g. of mixed keto-acids. The eutectic m. p. 42·4°, the b. p., and the analysis showed the absence of undecynoic acid [Found in product B (see table) : C, 66·0; H, 9·9. Calc. : C, 66·0; H, 10·0%]. Modifications of this procedure are indicated in the table.

Effect of the process of isolation on the yield and composition of the product. The finely ground mixture of keto-acids (3·5 g., m. p. 43·65°, 50·8% of 10-keto-acid) was dissolved in sulphuric acid (30 c.c. of 85% at 8°), and after 6 hours at room temperature the solids were recovered as described above. The distilled product (3·2 g.) had m. p. 44·1°, raised by addition of 10-keto-acid (1%), which corresponded to 51·6% of 10-keto-acid, so the isolation process including distillation had raised the percentage of 10-keto-acid by 0·8%. A mixture of keto-acids (4·00 g.) distilled from the usual apparatus gave 3·82 g. of distillate, a loss of 0·18 g. without change of m. p.

In the table the yields given in parentheses are those obtained after applying the corrections for loss during the isolation process; the figures for the composition of the products have also been corrected.

Hydration with Mercuric Acetate in Acetic Acid.—General procedure. Undecynoic acid (5 g.) in acetic acid (10 c.c.) was added to a clear solution of mercuric acetate (from 14 g. of mercuric oxide) in hot acetic acid (125 c.c.); the mixture was kept for 8 hours at 90°, concentrated in a vacuum to 25 c.c., and the residue heated for 10 minutes at 70° with concentrated hydrochloric acid (30 c.c.) or with 25% sulphuric acid (30 c.c.). The ethereal extract of this mixture was saturated with hydrogen sulphide (to remove mercury compounds), filtered, and evaporated finally in a vacuum. From the residue (approx. 5 g.), distillation gave approx. 4·6 g. of keto-acids, b. p. 151—156°/0·1 mm. The products were faintly yellow, and the eutectic arrests were slightly low, 42·1—42·4°; analysis also indicated a trace of impurity (Found, in product M1 : C, 65·6; H, 10·2; *M*, 197. Calc.: C, 66·0; H, 10·0%; *M*, 200). Products M2 and M3 were lighter in colour and had *M*, 199. Any depression of the m. p. would give a lower percentage of 10-keto-acid by the direct reading, and this should be detected by adding sufficient 9-keto-acid to bring the composition on to the other branch of the curve, whereby a low percentage of 9-keto-acid and therefore indirectly a high percentage of 10-keto-acid would be indicated. M1 by direct reading contained 54% of 10-keto-acid; 0·4580 g. of 9-keto-acid added to 1·0158 g. of M1 gave a new mixture of m. p. 46·8° : whence 39·6% of 10-keto-acid in the mixture and 57·5% in M1. M3 by direct reading contained 54% of 10-keto-acid; 0·4757 g. of 9-keto-acid added to 1·5164 g. of M3 had m. p. 46·0°, whence 42% of 10-keto-acid in the mixture and 54% in M3.

Effect of the process of isolation. A solution of mixed keto-acids (3·95 g., 55·4% of 9-keto-acid, m. p. 45·0°) and mercuric acetate (from 10 g. of oxide) in acetic acid (110 c.c.) was kept for 6 hours at 90°. The product, recovered as described above (3·65 g.), had m. p. 44·9° (depressed by addition of 10-keto-acid), indicating 55·0% of 9-keto-acid, so no appreciable change in composition had occurred.

Expt.	Reagent.	Temp.	Time, hrs.	Yield, %.	M. p.'s.	9-Keto-acid, mols. %.
A	H_2SO_4, 85%	5—20°	20	87 (95)	45·8°	58
B	H_2SO_4, 80%	5—20	7	87 (95)	46·1	59
C	H_2SO_4, 80% + $HgSO_4$	,,	18	80 (90)	45·7	58
D	H_2SO_4, 80% + SO_2 + H_2	,,	4	85 (97)	46·35	60
E	H_2SO_4, 85% (19 c.c.) + AcOH (20 c.c.)	35	3	95 (99)	45·4	57
M1	$Hg(OAc)_2$ + AcOH	90	5	—	45·5, 46·3	46
M2	,, ,,	,,	,,	—	45·9, 46·8	45
M3	,, ,,	,,	8	84 (89)	45·5, 46·3	46
M4	,, ,,	40	60	86 (92)	45·3, 46·0	46·5

Admixture of Products of the Two Hydration Processes.—Product M2 (0·7 g.), m. p. 45·9° and 46·8°, was added to product A (0·8 g.), m. p. 45·8°. The new mixture had m. p. 43·1°, indicating that the compositions of the products were on opposite sides of the eutectic.

We are indebted to Mr. E. L. R. Mowat, B.A., for preparation of some of the undecynoic acid.

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY.

[*Received, July 3rd,* 1937.]