5. *The Hydration of Acetylenes. Part II. Penta-2-yne. Reactivity in Homologous Series.*

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The hydration of penta-2-yne with 80% sulphuric acid has been studied by estimation of the amounts of methyl propyl and of diethyl ketone produced. The results along with those of the hydration of Δ^9-undecynoic acid show that in the reaction

$$2CH_3\cdot C\vdots CR + 2H_2O \longrightarrow CH_3\cdot CH_2\cdot COR + CH_3\cdot CO\cdot CH_2R$$

the acetylenes display increasing reactivity with increasing length of alkyl chain (Homologous Series Reactivity, Type III; Abraham, Mowat, and Smith, J., 1937, 948). This is due to the increase of negativity of carbon attached to alkyl (general effect), and the steric or orientation effect is considered to act equally on both the carbon atoms.

IN Part I (Sherrill and Smith, J., 1937, 1501) the hydration of Δ^9-undecynoic acid ($CH_3\cdot C\vdots C\cdot[CH_2]_7\cdot CO_2H$) with sulphuric acid was shown to give 59% of 9-keto- and 41% of 10-keto-undecoic acid. It was hoped to obtain a comparable analysis of the hydration products of penta-2-yne, but none of the methods available gave accurate results and the hydration was accompanied by some polymerisation.

$$CH_3\cdot C\vdots C\cdot C_2H_5 + H_2SO_4,H_2O \longrightarrow CH_3\cdot CH_2\cdot CO\cdot C_2H_5 \quad (52\%)$$
$$CH_3\cdot C\vdots C\cdot[CH_2]_7\cdot CO_2H + H_2SO_4,H_2O \longrightarrow CH_3\cdot CH_2\cdot CO\cdot[CH_2]_7\cdot CO_2H \quad (59\%)\ ^1$$
$$CH_3\cdot CH:CH\cdot C_2H_5 + HBr \longrightarrow CH_3\cdot CH_2\cdot CHBr\cdot C_2H_5 \quad (53\%)\ ^2$$
$$CH_3\cdot CH:CH\cdot[CH_2]_7\cdot CO_2H + HBr \longrightarrow CH_3\cdot CH_2\cdot CHBr\cdot[CH_2]_7\cdot CO_2H \quad (50\%)\ ^3.$$

[1] Part I, *loc. cit.* [2] Lauer and Stodola, *J. Amer. Chem. Soc.*, 1934, **56**, 1215.* [3] Abraham, Mowat, and Smith, *loc. cit.*

The first two results above show that in the hydration of a series of acetylenes, $CH_3\cdot C\vdots CR$, with sulphuric acid the relative reactivity of C attached to alkyl *increases* with increasing length of the alkyl chain; this is an example of homologous series reactivity, type III (Abraham, Mowat, and Smith, *loc. cit.*).

Consideration of series in which there is a large fall in reactivity in passing from CH_3X to C_2H_5X . . . C_4H_9X as in the *n*-alkyl iodides when reacting with sodium phenoxide (Segaller, J., 1913, **103**, 1154) shows that these are cases in which both a general effect and a steric or orientation factor should exist. Thus in the formation of phenol ethers ($R\cdot CH_2I$ + NaOPh) the tendency of the methylene group to attach itself to the oxygen

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* The value 79% of 3-bromopentane found by Lucas and Moyse (*ibid.*, 1925, **47**, 1459) has now been withdrawn (Lucas and Prater, *ibid.*, 1937, **59**, 1682; see also Sherrill and Matlack, *ibid.*, p. 2134).

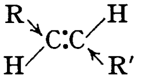
atom should be lessened by the general effect of the larger *n*-alkyl group (which will make the α-methylene group more negative); but much more important should be the steric factor: the probability that the α-methylene group will be in a suitable position for reaction to occur will be greatly diminished as R changes from hydrogen to *n*-propyl. That the differences in charge between the carbon atoms attached to iodine are small is shown by the dipole moments of vapours of alkyl iodides (Groves and Sugden, J., 1937, 158):

R =	H.	Me.	Et.	*n*-Pr.
μ =	1·64	1·87	2·01	2·08 e.s.u. × 10^{-18}

(The differences are smaller for a series of bromides or chlorides.)

Owing to the polarisability of triple bonds it is possible for the alkyl groups in acetylenes to induce by their (opposed) general effects sufficient polarity to influence the composition of the product of hydration with sulphuric acid. Allowing for errors of ± 3% in both the results quoted, it seems that in the olefins the polarisation is insufficient to influence the addition of hydrogen bromide; there is no information as to whether it can affect the hydration with sulphuric acid. In those cases where the proportions of two addition products are being measured and both alkyl groups are in the same molecule it is obvious that the *orientation factor* need not be considered: it may affect the reactivity of the molecule as a whole, but should not affect the *relative* reactivity of the unsaturated carbon atoms.

A factor which may be of importance is the angle through which the effects are directed towards the double or triple bond. If it is considered that in the olefins the polarisation



$R \rightarrow C⋮C \leftarrow R'$

is altered by this angle, the effects should be 0·58 $\left(= \cos\frac{109° \; 28'}{2}\right)$ of those in the acetylenes.

EXPERIMENTAL.

Penta-2-yne.—A solution of β-amylene (250 g., Messrs. British Drug Houses Ltd.) in carbon disulphide (300 c.c.) was stirred in a freezing mixture while bromine (570 g.) in carbon disulphide (400 c.c.) was added. After the solvent had been removed the dibromo-compound was distilled at 90°/14 mm. (yield, 750 g.). Powdered potassium hydroxide (300 g.) and alcohol (400 c.c. of 98%) were stirred in a 3-neck flask heated in an oil-bath until most of the potash was in solution. The flask was provided with a mercury seal, a dropping-funnel, and a condenser kept at 40° to return alcohol. Vapour which passed this condenser was led to a second condenser kept at 0°.

A vigorous reaction was kept going by dropping in dibromopentane (200 g.) and it was possible by stirring to obtain a regular distillation of pentyne. When all the bromo-compound had been added, the temperature of the oil-bath was raised and alcohol allowed to distil until the total had reached 150 c.c. The residue in the reaction flask was largely diluted with water, and the bromopentene layer separated for heating with alcoholic potassium hydroxide in sealed tubes (Faworsky, *J. pr. Chem.*, 1888, **37**, 382). Fractionation of the pentyne distillate gave 35—45 g., b. p. 40—60°, containing apparently more penta-1-yne than penta-2-yne.

Conversion into Penta-2-yne.—The crude pentyne (15 c.c.) was heated with concentrated alcoholic potassium hydroxide solution (6 c.c.) in a sealed tube for 20 hours at 200°. The products from several experiments were well washed with water to remove alcohol and dried. Fractionation with a Young column easily separated penta-1-yne from penta-2-yne. Fraction (i), b. p. 36—55·0° (15 g.), and fraction (ii), 55·0—55·5° (14 g.), gave precipitates with alcoholic silver nitrate; fractions (iii), 55·5—55·6° (9·5 g.), (iv) main fraction, 55·6°/760 mm. (15 g.), and (v), 55·6—56·0° (6·0 g.), gave no precipitate with silver nitrate. There was a residue of polymerised material (30—40 g.). Fractions b. p. 55—55·5° were used for preliminary experiments and fractions b. p. < 55° were reheated with alcoholic potassium hydroxide.

Diethyl Ketone.—The commercial product was distilled; the main fraction (b. p. 101·8—102·2°) yielded a semicarbazone, m. p. 137—138°, raised by two crystallisations from methyl alcohol to 139—140°. Dilthey (*Ber.*, 1901, **34**, 2122) gives m. p. 139°. A specimen of diethyl ketone from propionitrile and ethylmagnesium bromide boiled at 101—102° and yielded a semicarbazone of m. p. 139°. The *p*-nitrophenylhydrazone melted at 140—141° (van Ekenstein and Blanksma, *Rec. trav. chim.*, 1903, **22**, 435, give m. p. 141°).

Methyl Propyl Ketone.—A sample boiling constantly at 102·0° gave a crude semicarbazone, m. p. 96°, which after four crystallisations from methyl alcohol gave a small yield of plates, m. p. 113°. Bouveault and Bongert (*Bull. Soc. chim.*, 1902, **27**, 1083) give m. p. 112°. Benzene was of little use for the purification and it was possible that the crude semicarbazone contained some of the yet unknown geometrical isomeride. A specimen of the ketone from ethyl ethylacetoacetate also gave a crude semicarbazone, m. p. 96°, and after recrystallisation, 111°. The crude *p*-nitrophenylhydrazone melted at 108—110° and after many crystallisations from alcohol, alcohol–pyridine, and alcohol–acetic acid it melted at 116°. Fischer and Tropsch (*Ber.*, 1923, **56**, 2433) give m. p. 116—117°.

Mixtures of the Semicarbazones of Pentan-2- and -3-one.—Preliminary determinations showed that the system was of the eutectic type and that mixtures containing more than 70% of the semicarbazone of pentan-3-one melted with slight decomposition. The curve from the following m. p.'s (thermometer in the liquid) was used in the analysis of mixtures :

Pentan-3-onesemicarbazone, mols. % ...	62·7	60·0	55·0	50·0	47·0
M. p.	116·1°	113·5°	109·0°	104·3°	101·4°

Mixtures of the p-*Nitrophenylhydrazones of Pentan-2- and -3-one.*—The curve was drawn from the following points (thermometer in the liquid) :

Pentan-3-one-*p*-nitrophenylhydrazone, mols. %	64·3	58·1	50·0	43·4
M. p.	122·1°	118·1°	112·2°	106·5°

Hydration of Penta-2-yne.—The following method was finally adopted, as it gave high yields and only a little polymerisation occurred. Sulphuric acid (16 c.c. of 80%) was cooled to 0° in a 50 c.c. stoppered flask. Penta-2-yne (4·0 c.c., 2·9 g.), cooled to 0°, was added in one portion, and the flask shaken vigorously while cooled with ice-water. After 8 minutes the smell of acetylene was replaced by the pleasant smell of ketones, and after a total of 10 minutes the mixture was poured on ice. The ketones were carefully extracted (four extractions), a total of 20—30 c.c. of purified light petroleum (b. p. 50—60°, freed from olefins) being used (extraction with ether led to losses, benzene formed emulsions, and chloroform reacted with the ketones). In some experiments the extract was distilled at about 250 mm. pressure from a small flask, and the vapour condensed in receivers cooled in a freezing mixture. Traces of high-boiling liquid were left in the flask.

Analysis of the Hydration Products.—Physical methods of analysis such as the refractive index method were ruled out by the similarity of physical properties of the ketones.

Pringsheim and Gorgas (*Ber.*, 1924, **57**, 1361) have recommended measurement of the rate of oxime formation, but this did not appear to be a sufficiently accurate process. Although methyl propyl ketone reacted enormously faster than diethyl ketone with sodium bisulphite solution, the reaction was incomplete even in presence of a large excess of bisulphite. Precipitation of the 2 : 4-dinitrophenylhydrazones gave products slightly contaminated with the reagent. Finally the semicarbazones and *p*-nitrophenylhydrazones were used and corrections were applied for the greater solubility of the methyl propyl ketone derivatives.

Analysis as Semicarbazones.—The extract of the products of hydration was shaken for 48 hours in a stoppered bottle with semicarbazide hydrochloride (6·0 g.) and potassium acetate (7·5 g.) in water (10 c.c.). The liquid was then filtered into a separating funnel. The aqueous layer was extracted with light petroleum and then all the petroleum liquors were evaporated. In order to remove semicarbazide the total solid residues were ground with water (10 c.c.), collected, and dried in a vacuum. An alternative method of washing was to dissolve the semicarbazones in chloroform (18 c.c.) and to extract the solution rapidly twice with water (10 c.c. each time). Experiments carried out with a 50/50 mixture of the ketones showed that the first method of isolation and washing caused an average rise of 2·6° in the m. p., and the second method a rise of 1·2°. The semicarbazones were slowly hydrolysed by water.

Hydration A gave 4·94 g. (81% yield) of washed semicarbazones (Found : N, 29·7. Calc., 29·4%), m. p. 106·5° (corrected for solubility, 103·9°), indicating 49·5% of diethyl ketone.

Hydration B (the extract of the ketones was distilled) gave 4·7 g. (78% yield) of semicarbazones (Found : N, 29·6), m. p. 108° (corrected 106·8°), indicating 52·5% of diethyl ketone.

Analysis as p-*Nitrophenylhydrazones.*—Tests were made on a solution containing 55 parts of diethyl ketone to 45 parts of methyl propyl ketone (4 g. of mixture in 25 c.c. of light petroleum). The solution of the ketones (4·0 c.c.) was added to a clear solution of *p*-nitrophenylhydrazine (1·7 g.) in acetic acid (6 c.c.) and water (4 c.c.) and the mixture was left for 3 days with frequent periods of shaking on a machine. Water (10 c.c.) was then added, and the mixture left for 1 hour. After the light petroleum had been removed carefully in a vacuum, the liquid was filtered, and the solid washed with acetic acid (twice with 5 c.c. of 20%) and then with water (5 c.c.). It was dried in a vacuum over potassium hydroxide. From the melting point, 118° (119° for the product of a second experiment) a composition of 59% of diethyl ketone was indicated, so a correction of — 4% had to be applied. (The yields were 1·9 and 2·05 g., 78 and 86% respectively.) A similar test on a 50/50 mixture of the ketones in light petroleum gave a product, m. p. 116°, indicating a correction of — 5%.

Hydrations were carried out as in experiments A and B, the product being extracted with light petroleum and the volume made up to 25 c.c. For analysis 4—5 c.c. of the solution were shaken with *p*-nitrophenylhydrazine as described above.

Hydration C. 4·0 C.c. of extract yielded 1·5 g. of solid (Found : N, 19·2. Calc., 19·0%). The m. p. 115·2° (54% of the diethyl ketone derivative) indicated a corrected value of 50% of diethyl ketone.

Hydration D. The extract of the ketones was distilled before the volume was made up to 25 c.c. From 4·5 c.c. of this extract 1·6 g. of *p*-nitrophenylhydrazones were obtained (Found : N, 19·2%). The m. p. 116·5° (56·5%) indicated 52% of diethyl ketone.

Hydration E. The sulphuric acid solution of the ketones was poured on ice, the mixture neutralised with 30% sodium hydroxide solution, and steam passed. The ketones were carefully extracted from the distillate (60 c.c.) with light petroleum (25 c.c.). 4·0 C.c. of this extract yielded 1·4 g. of *p*-nitrophenylhydrazones, m. p. 118° (58%), indicating 54% of diethyl ketone.

Hydration.	Method of analysis.	Diethyl ketone, mols. %.	Hydration.	Method of analysis.	Diethyl ketone, mols. %.
A	Semicarbazones	49·5	D	*p*-Nitrophenylhydrazones	52
B	,,	52·5	E	,, ,,	54
C	*p*-Nitrophenylhydrazones	50	Mean		52

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