

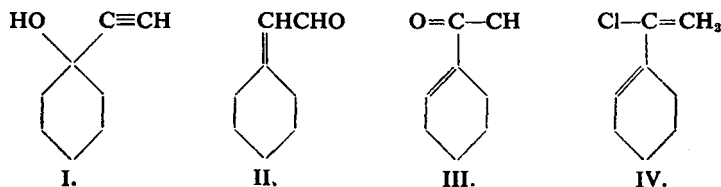
A NOTE ON RUPE'S REARRANGEMENT

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RUPE, *et al.*¹ described a rearrangement in which 1-ethynylcyclohexanol-1 (I) was heated with 85 per cent. formic acid. They asserted that the compound obtained was cyclohexylidene acetaldehyde (II) on the evidence of a positive colour test with Schiff's reagent, but the physical constants of its hydrogenated product were not quite those expected. On the other hand, ozonolysis of the compound gave not cyclohexanone but adipic acid. It was later shown by Fischer and Loewenberg² that the compound was actually 1-acetyl-cyclohexene-1 (III). Further, it was established by Hurd and Jones³ that, in an analogous manner, 1-ethynylcyclohexanol-1 was converted by thionyl chloride in presence of pyridine into 1- α -chlorovinyl-cyclohexene-1 (IV).



Hurd and Christ⁴ repeated Rupe's rearrangement and the product, boiling at 60° to 64°C./4 mm., was identical in every respect with the 1-acetylcyclohexene-1 prepared by Darzen's method from acetyl chloride and cyclohexene. Both gave a semicarbazone melting at 220° to 221°C. and no depression was observed on determining a mixed melting-point.

On attempted dehydration of 1-ethynylcyclohexanol-1 with anhydrous oxalic acid, Levina and Vinogradova⁵ obtained the same 1-acetyl-cyclohexene-1, but Bergmann and Bergmann⁶ reported cyclohexanone and cyclohexenylacetic acid as the product.

In this laboratory, experiments were carried out under similar conditions. On heating 1-ethynylcyclohexanol-1 with anhydrous oxalic acid at 120°C. a vigorous reaction soon set in, after the subsidence of which the mixture was heated for another 1½ hours and the product isolated by extraction with benzene and fractionation. Invariably, a yield of about 40 per cent. of 1-acetylcyclohexene-1 was obtained together with a little of a low-boiling fraction, the residue in the flask being polymerised tarry matter. The main fraction showed the following constants b.pt. 63° to 64°C./6mm., $n_D^{23^\circ C.}$ 1.4903, $n_D^{18^\circ C.}$ 1.4928, $d_4^{20^\circ C.}$ 0.9678, EM_D 0.79, and gave no colour with Schiff's reagent after standing overnight, although it reduced Fehling's solution on shaking in a boiling water-bath. It gave a

semicarbazone (from acetone/chloroform), melting at 210°C. and a 2:4-dinitrophenylhydrazone (from acetone/chloroform), melting at 204° to 205°C. Its ultra-violet absorption spectrum was taken and is shown in Figure 1; λ max. 234 $m\mu$, $E_{1\text{ cm.}}^{1\text{ per cent.}}$ 957, $\log. \epsilon$ 4.075 (in absolute alcohol). Additional direct proof of the methyl ketone structure was obtained by a positive iodoform test.

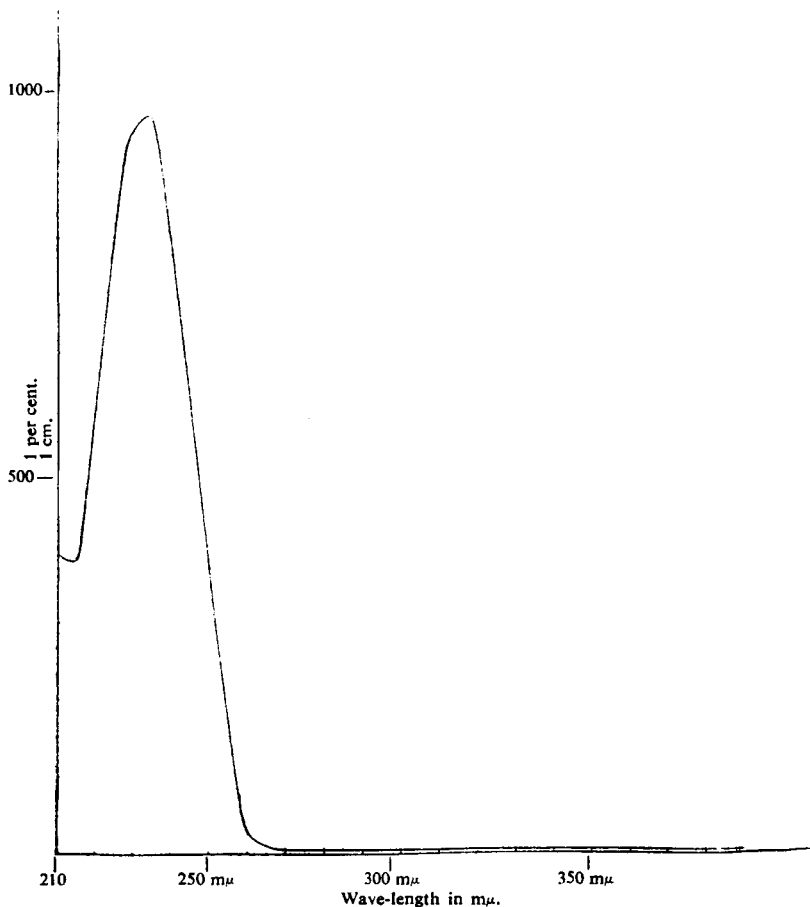
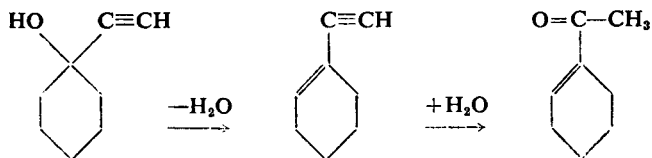


FIG. 1.

An attempt was then made to explain the mechanism of this reaction. As both 85 per cent. formic acid and anhydrous oxalic acid are dehydrating agents, it was postulated that the reaction proceeded by a primary dehydration and a subsequent hydration:



RUPE'S REARRANGEMENT

This was substantiated by subjecting 1-ethynylcyclohexene-1 to similar treatment with 85 per cent. formic acid, and with anhydrous oxalic acid plus a little water. In the former case a 52 per cent. yield and in the latter a 29.5 per cent. yield, of the 1-acetylcyclohexene-1 were obtained. The product, on analysis and determination of the physical constants, gave the required figures and no depression of the melting-point was observed when the semicarbazone and the 2:4-dinitrophenylhydrazone obtained from it were mixed with those obtained as described above. Absorption maximum 234μ , and $E_{1\text{ cm.}}^{1\text{ per cent.}}$ were 958 and 954 respectively (in absolute alcohol).

EXPERIMENTAL

1. *Rearrangement of 1-ethynylcyclohexanol-1 by heating with anhydrous oxalic acid.*—1-ethynyl-cyclohexanol-1 (13.0 g.) was mixed with anhydrous oxalic acid (9.0 g.) and the mixture was heated under a reflux condenser in an oil bath at 120°C . A vigorous reaction soon set in and the heating was interrupted by lifting the flask out of the oil bath. When the reaction had subsided the blackish mixture was heated at 120°C . for another $1\frac{1}{2}$ hours. After cooling, the product was extracted with benzene and the benzene extract was washed and dried. On fractionation, the fraction distilling at 60° to $70^{\circ}\text{C}/6$ to 10 mm. was collected, which on redistillation, mainly distilled at 63° to $64^{\circ}\text{C}/6\text{ mm. Hg. pressure}$. Yield: 5 g. (38 per cent.). Found: C, 77.75; H, 9.87 per cent.; $\text{C}_8\text{H}_{12}\text{O}$ requires C, 77.40; H, 9.75 per cent. $n_{\text{D}}^{16^{\circ}\text{C.}} 1.4928$, $n_{\text{D}}^{23^{\circ}\text{C.}} 1.4903$, $d_4^{20^{\circ}\text{C.}} 0.9678$; molecular refraction, according to 1-acetyl-cyclohexene-1: found 37.28; calculated 36.49, $\text{EM}_{\text{D}} 0.79$. It gave no precipitate with ammoniacal silver nitrate, gave no active hydrogen (Zerewitinoff); did not restore Schiff's reagent on standing overnight, but reduced Fehling's solution on heating in a boiling water-bath with shaking. To a few drops of the product in a test tube, 5 ml. of a solution of iodine in potassium iodide and 2 ml. of 20 per cent. sodium hydroxide solution were added, a yellow crystalline precipitate formed was identified as iodoform. The semicarbazone, recrystallised from a mixture of chloroform and acetone melted at 210°C . Found: C, 59.86; H, 8.47; N, 22.60 per cent. $\text{C}_9\text{H}_{15}\text{ON}_3$ requires C, 59.64; H, 8.34; N, 23.19 per cent. The 2:4-dinitrophenylhydrazone, recrystallised from a mixture of chloroform and acetone, melted at 204° to 205°C . Found: C, 55.26; H, 5.44; N, 18.1 per cent. $\text{C}_{14}\text{H}_{16}\text{O}_4\text{N}_4$ requires C, 55.26; H, 5.30; N, 18.42 per cent. Absorption spectrum: max. $234\text{ m}\mu$, $E_{1\text{ cm.}}^{1\text{ per cent.}} 957$, $\log \epsilon 4.075$ (in absolute alcohol).

2. *Addition of water on to 1-ethynylcyclohexene-1 in presence of oxalic acid.*—1-ethynylcyclohexene-1 (5 g.) was heated with anhydrous oxalic acid (3.5 g.) and water (0.5 g.) in exactly the same manner as before. On fractionation of the benzene extract of the product, the fraction 55 to $60^{\circ}\text{C}/7$ mm. Hg pressure was collected, which on redistillation gave a main distillate at $58^{\circ}\text{C}/5$ mm. Hg. pressure. Yield, 1.7 g. (29.5 per cent.) $n_{\text{D}}^{18^{\circ}\text{C.}} 1.4923$, $n_{\text{D}}^{23^{\circ}\text{C.}} 1.4900$. Reactions were found

to be the same as before. Found: C, 77.23; H, 9.74 per cent. $C_8H_{12}O$ requires C, 77.40, H, 9.75 per cent. The semicarbazone and 2:4-dinitrophenylhydrazone showed the same melting-point, and mixed melting-points showed no depressions when mixed with the corresponding derivatives obtained from experiment 1. Absorption maximum $234 m\mu$, $E_{1\text{cm.}}^{1\text{ per cent.}}$ 954 (in absolute alcohol).

3. *Addition of water to 1-ethylcyclohexene-1 in presence of 58 per cent. formic acid.*—The reaction was carried out according to the conditions given by Rupe¹ for his rearrangement of 1-ethynylcyclohexanol-1. 1-Ethynylcyclohexene-1 (5 g.) was refluxed with 85 per cent. formic acid (40 ml.) in an oil bath at 120°C . A vigorous but smooth reaction started and the mixture turned dark coloured. After further heating for $2\frac{1}{2}$ hours, the acid was neutralised with sodium carbonate and the product was extracted with benzene. The benzene extract was then washed and dried. On fractionation a distillate was collected between 50 and $58^\circ\text{C}/7$ mm. Hg pressure which on redistillation distilled mainly at $58^\circ\text{C}/5$ mm. Hg pressure. Yield: 3 g. (52 per cent.) $n_D^{18^\circ\text{C}}$ 1.4925; $n_D^{23^\circ\text{C}}$ 1.4901. The reactions were found to be identical with those previously recorded above. Found: C, 77.13; H, 9.60 per cent. $C_8H_{12}O$ requires C, 77.40; H, 9.75 per cent. The semicarbazone and 2:4-dinitrophenylhydrazone gave the same melting-points as those from experiments 1 and 2 and the mixed melting-points showed no depression.

Absorption maximum: $234 m\mu$, $E_{1\text{cm.}}^{1\text{ per cent.}}$ 958 (in absolute alcohol).

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