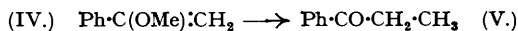
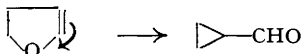


The possibility that the cyclopropane ring had opened under the drastic conditions of reaction cannot be ruled out: further experiments are necessary to settle this question.

In the experiments with the nitrile it was noticed that, as the temperature approached 400°, the amount of 2:3-dihydrofuran increased; thereafter up to 500° it decreased and the aldehyde (II) appeared in increasing quantities. It is, therefore, not illogical to suppose that the aldehyde was a rearrangement product of the furan; the molecules are, of course, isomeric. There is support for this hypothesis if 2:3-dihydrofuran can behave, as its structure would suggest, like a vinyl ether. Some vinyl ethers are known to rearrange to carbonyl compounds on heating. For example, Claisen (*Ber.*, 1896, **29**, 2931) showed that α -methoxystyrene (IV) was converted into propiophenone (V). In this example an alkyl group migrates from oxygen to carbon.



In dihydrofuran a similar migration would mean shrinkage of the ring from five to three members:



These reactions will be studied further.

EXPERIMENTAL.

I. *Apparatus*.—The arrangement of the furnace and catalyst tube was as described in the preceding paper.

II. *Preparation of Catalysts*.—(a) *Silica gel*. Commercial silica gel was prepared as described on p. 55

(b) *Alumina on pumice*. Granulated pumice (8–16 mesh) was impregnated with aqueous (40%) aluminium nitrate, dried at 80°, and then heated slowly to 400° in a stream of air in the catalyst tube.

(c) *Calcium phosphate*. Calcium phosphate, ammonium phosphate, and graphite were mixed with water, heated to dryness, and the cake broken and packed in the catalyst tube. The catalyst was heated in nitrogen at 385° before use (cf. B.P., 317,500).

(d) *Sodium phosphate*. Pumice (8–16 mesh) was impregnated with a hot solution of sodium dihydrogen phosphate (120 g.) and phosphoric acid (glacial, 15 c.c.) in water (85 c.c.), and dried by raising the temperature slowly to 300° in a stream of air (cf. B.P., 506,038).

In some experiments the catalyst tube was filled with earthenware rings to try the effect of a relatively inert material with little, if any, catalytic properties.

III. *Preparation of Materials*.—*Furoic acid*. Furfuraldehyde (technical, 768 g., 8 g.-mols.) was treated with sodium hydroxide as described in *Organic Syntheses* (Coll. Vol. I, p. 270). The yield of the acid in different experiments varied between 280 and 340 g. (63–73%), m. p. 130–131°. Some furfuraldehyde was recovered from the ethereal extract by distilling it at 165–171°, and extracting the aldehyde from the distillate (furfuryl alcohol) by shaking it with aqueous sodium hydrogen sulphite.

Furoyl chloride, b. p. 174°, was prepared in 95% yield by the action of thionyl chloride on the acid. Reaction with aqueous ammonia gave the amide, m. p. 138–140°, b. p. 145–148°/11 mm. Methyl furoate, b. p. 178–180°, resulted in 70% yield either by reaction of the chloride with methyl alcohol or by direct esterification of the acid.

Tetrahydrofuroic acid (cf. Weinhaus and Sorge, *Ber.*, 1913, **46**, 1929). Furoic acid (m. p. 130–131°; 200 g.), dissolved in ammonia (d 0.880; 150 c.c.) and water (350 c.c.), was introduced into a rotating Bergius converter (capacity 2 l.) along with Raney nickel (20 g.) and hydrogen (93 atm./20°). Reduction was complete in 5 hrs. at 130–150°. A weighed sample of the resulting solution after filtration from catalyst was boiled with excess of standard alkali and back-titrated with acid (phenolphthalein as indicator). This showed that recovery of organic acid was about 94%. Acidification showed the absence of more than 5% of unreduced furoic acid. Tetrahydrofuroic acid was isolated in 60% yield by strongly acidifying the solution of the ammonium salt and repeatedly extracting it with ether. A better yield (90%) was obtained by distilling the methyl ester with an equal volume of 2N-hydrochloric acid until methyl alcohol ceased to be evolved. The residue was then distilled in a vacuum; b. p. 118–120°/18 mm.

Methyl tetrahydrofuroate. Reduction of a methyl-alcoholic solution of methyl furoate with a Raney nickel catalyst (nickel on kieselguhr was less effective) took 5 hrs. at 120°. The product, 90% yield, b. p. 77–78°/15 mm., was completely miscible with cold water.

Tetrahydrofuroamide. A solution of ammonium tetrahydrofuroate was evaporated to dryness in a vacuum, and the residue heated to 220–230° in a stream of ammonia so that water could distil off. The residue was then distilled, b. p. 134–136°/10 mm.; yield 76%. The aqueous distillate from the ammonia treatment was distilled separately to give a further 5% yield of the amide.

Under these conditions of amide formation, ammonium furoate gave a product (probably a complex of acid and amide), b. p. 160°/11 mm. The ammonia treatment thus served to separate any remaining unreduced furoic acid.

Tetrahydrofuronitrile. Attempts to dehydrate the amide by carbonyl chloride at high temperatures failed. Smooth dehydration to the nitrile was, however, effected by passing the vapour of the amide over a silica gel or sodium phosphate catalyst. The amide was contained in a specially designed dropping-funnel and was kept liquid by wrapping the funnel with lead tubing carrying steam. Instead of a tap, the funnel had an internal valve made by grinding a tapered glass rod to fit the exit neck of the funnel. The rod extended through a rubber gasket in the upper neck of the funnel. In this way the use of tap lubricant was obviated.

Dehydration of amide. (a) Over silica gel. An amide input of 10 g./hr. and nitrogen carrier (2 l./hr.) gave at 360–400° a product consisting of nitrile and 2:3-dihydrofuran, identified by conversion into γ -hydroxybutaldehyde-2:4-dinitrophenylhydrazone (see previous paper), together with some hydrogen cyanide. The catalyst deteriorated in use but was readily reactivated by treatment with a stream of air at 550–580°.

As the temperature was reduced below 330° the consumption of amide and the amount of dihydrofuran produced both decreased. After allowance for recovered amide, the yield of nitrile and consumption at various temperatures were as follows, a freshly reactivated catalyst being used for each experiment: 290°, 74%, 60%; 310°, 55%, 80%; 330°, 40%, 90%. At the highest temperature in this series (330°) about 8% of the total product consisted of a mixture, b. p. 50–62°, of di- and tetra-hydrofuran containing 55% of the former.

(b) Over sodium phosphate. This catalyst at 400° gave a 90% yield of pure nitrile with an amide consumption of 50–85%.

Tetrahydrofuronitrile was a colourless, mobile liquid, immiscible with water; b. p. 71–73°/10 mm. (Found: C, 61.7; H, 7.3; N, 14.4. Calc. for C_5H_7ON : C, 61.9; H, 7.3; N, 14.4%). The only other preparation recorded is that of Williams (*Ber.*, 1927, **60**, 2509), who dehydrated the oxime with acetic anhydride.

IV. Reactions of Tetrahydrofuronitrile Vapour over Various Catalysts.—(a) *Earthenware rings*. With nitrogen (2 l./hr.) as carrier gas, 70% of the nitrile was recovered at 450°. About 10% of the product consisted of impure 2:3-dihydrofuran.

(b) *Silica gel*. At 500° the nitrile gave a product containing about 10% of b. p. 130—140°, 20% of 2:3-dihydrofuran-tetrahydrofuran mixture (48% of former), and 10% of unchanged nitrile. The fraction, b. p. 130—140°, had a sweet odour reminiscent of an aliphatic nitrile (Found: C, 74.75; H, 8.15; N, 14.3. Calc. for C_6H_7N : C, 75.9; H, 6.3; N, 17.7%). It was colourless when freshly distilled. A similar liquid was obtained in experiments with ammonium tetrahydrofuroate (see below).

(c) *Sodium phosphate*. Little reaction was evident below 450°. At this temperature about 10% of the nitrile reacted to give mainly hydrogenated furans. At 500° the reaction product contained hydrogen cyanide, only a little hydrogenated furans, and mainly a liquid, b. p. 42—44°/14 mm., which gave a copious precipitate of Prussian-blue on treatment with sodium hydroxide and ferrous sulphate, followed by heating and acidification. The liquid seemed to be a cyanohydrin, since reaction with 2:4-dinitrophenylhydrazine dissolved in 2*N*-hydrochloric acid gave a precipitate which crystallised from ethyl acetate-ethyl alcohol in orange-red prisms, m. p. 173—175° (Found: C, 48.0; H, 4.2; N, 22.2. $C_{10}H_{10}O_5N_4$ requires C, 48.0; H, 4.0; N, 22.4%). This was shown to be cyclopropanealdehyde-2:4-dinitrophenylhydrazone by mixed m. p. with an authentic specimen, m. p. 172—174°, synthesised as described below. The *p*-nitrophenylhydrazone crystallised from ethyl alcohol in brown needles, m. p. 126—127° (Found: C, 59.1; H, 5.2; N, 20.2. $C_{10}H_{11}O_5N_3$ requires C, 58.5; H, 5.4; N, 20.5%), undepressed on admixture with an authentic specimen (m. p. 126—127°).

Identification of 2:3-Dihydrofuran.—The low-boiling fractions from the above experiments were collected, dried over potassium hydroxide, and distilled. The fraction, b. p. 53—58° (Found: C, 69.2; H, 8.95. C_4H_6O requires C, 68.6; H, 8.6%), reacted rapidly with bromine in aqueous acetic acid solution and dissolved with heat evolution on treatment with 0.1*N*-sulphuric acid. This solution with 2:4-dinitrophenylhydrazine hydrochloride solution gave a golden-yellow crystalline hydrazone, m. p. 114—115°, shown by mixed m. p. to be derived from γ -hydroxybutaldehyde (cf. p. 56). Quantitative precipitation showed that the liquid, b. p. 53—58°, contained about 50% of 2:3-dihydrofuran. The remainder was probably tetrahydrofuran.

V. *Catalytic Dehydration of Ammonium Tetrahydrofuroate*.—An aqueous solution (50%) of ammonium tetrahydrofuroate containing excess of ammonia was introduced into the catalyst chamber at a rate of 10 c.c./hr. Ammonia (2 l./hr.) was also admitted as carrier.

(a) *Over earthenware rings*. At 500° a product was obtained which behaved like an equimolecular mixture of tetrahydrofuroic acid and amide. The crude material was analysed [Found: C, 50.15; H, 7.2; N, 5.4; *M* (cryoscopic in benzene), 155; equiv. by titration, 295. Calc. for $(C_4H_7O) \cdot CO_2H, (C_4H_7O) \cdot CO \cdot NH_2$: C, 51.9; H, 7.4; N, 6.1%; *M*, 231].

(b) *Over silica gel*. At 400° the results were like those with earthenware rings at 500°. At 500—600°, however, the product contained a water-insoluble liquid, b. p. 130—140°/760 mm., similar to that (C_6H_5N) obtained by passage of tetrahydrofuronitrile vapour over silica gel (Section IV). Higher-boiling fractions of the reaction product, b. p. 70—75°/16 mm. [Found: C, 61.55; H, 7.05; N, 9.0; *M* (cryoscopic in benzene), 80 approx. Calc. for C_6H_7ON : C, 61.9; H, 7.3; N, 14.4%; *M*, 97], appeared to consist largely of tetrahydrofuronitrile.

VI. *Reactions of Methyl Tetrahydrofuroate Vapour*.—The ester was passed into the catalyst chamber at a rate of 20 g./hr.

(a) *Over sodium phosphate*. Between 10 and 50% of the ester was consumed at temperatures between 450° and 550°. Variation of conditions, temperature, and carrier gas (nitrogen, carbon dioxide) appeared to have but little influence on the result. There were indications, however, that a fresh catalyst gave a higher consumption. Carbon monoxide was identified in the issuing gases. The reaction product (20—30% yield by weight, after allowance for recovered ester) had b. p. 45—90°. A sample (10.8 c.c.) of this liquid was distilled and divided into four fractions. One fraction, b. p. 55—65° (1.8 c.c.) gave methyl 3:5-dinitrobenzoate, m. p. 106—107° (and mixed m. p.), on treatment with dinitrobenzoyl chloride in pyridine. Another fraction, b. p. 75—90° (2.3 c.c.), was treated with aqueous dinitrophenylhydrazine and the precipitate recrystallised from ethyl acetate; it formed orange-red prisms, m. p. 172—175° (Found: C, 47.9; H, 4.0; N, 22.1%), identified as the derivative of (II) by mixed m. p. The amount of derivative indicated that about half the fraction was this aldehyde. The yield on consumed ester, therefore, was 2—3%.

The fraction, b. p. 45—55° (4.3 c.c.), after being shaken with aqueous bisulphite, was shown to contain 2:3-dihydrofuran by preparation of γ -hydroxybutaldehyde-2:4-dinitrophenylhydrazone, m. p. 116—118° (Found: C, 44.3; H, 4.3; N, 20.4. Calc. for $C_{10}H_{11}O_5N_4$: C, 44.7; H, 4.5; N, 20.9%). The remaining fraction, b. p. 65—75° (2.0 c.c.), had, like the others, a pungent smell recalling crotonaldehyde. It was treated with hydrogen in the presence of Adams's platinum catalyst. Only 85 c.c. were absorbed but the pungent odour had disappeared. Brady's reagent then precipitated the 2:4-dinitrophenylhydrazone of (II), m. p. 164—172°, identified by mixed m. p. The *p*-nitrophenylhydrazone had m. p. 126—133°. The dimedon derivative, m. p. 160—162°, was also prepared by precipitation from methyl-alcoholic solution (Found: C, 72.15; H, 8.8. Calc. for $C_{20}H_{28}O_4$: C, 72.3; H, 8.4%).

In another series of experiments the product, b. p. <100°, was treated with phenylhydrazine. Heat was evolved and water separated. Distillation gave the phenylhydrazone of (II), b. p. 140—150°/17 mm., white needles from ethyl alcohol, m. p. 68—69° (Found: C, 75.3; H, 7.3; N, 17.45. Calc. for $C_{16}H_{12}N_2$: C, 75.0; H, 7.6; N, 17.5%). It decomposed to a brown oil on standing for a few hours in air; analysis of the decomposition product showed that oxygen had been absorbed and nitrogen evolved (Found: C, 71.3; H, 6.75; N, 12.55%). The phenylhydrazone did not give a violet colour with ferric chloride solution, thus differentiating it from the phenylmethylpyrazoline from methyl vinyl ketone (see below).

In some of the pyrolyses butadiene was shown to be present by preparation of the tetrabromide.

(b) *Over alumina on pumice*. The results were similar to those with sodium phosphate.

(c) *Over silica gel*. At 325—350°, 65% of the ester was recovered unchanged. A little mixed hydrogenated furans were present. At 375°, 80% of the ester was consumed and a 30% yield (wt.) of product, b. p. <100°, was obtained. This contained 2:3-dihydrofuran and an aldehyde extracted by bisulphite solution. The solution gave a 2:4-dinitrophenylhydrazone, which crystallised from ethyl alcohol in orange-brown needles, m. p. 120—125° (Found: C, 47.7; H, 4.8; N, 22.25. Calc. for $C_{10}H_{11}O_5N_4$: C, 47.6; H, 4.8; N, 22.2%), showing (mixed m. p.) that the aldehyde was *n*-butaldehyde.

At 400°, with carbon dioxide as carrier gas, the ester gave a 35% yield (wt.) of liquid, b. p. <100°, and no unchanged ester. This contained some 2:3-dihydrofuran and about a third of its weight of the aldehyde (II), extracted by bisulphite. The dinitrophenylhydrazone had m. p. 169—174° after crystallisation from ethyl acetate.

(d) *Over calcium phosphate*. This catalyst was less effective than sodium phosphate but gave the same type of result.

(e) *Over marble chips*. With these in the catalyst tube, the only recognisable products at 450—475° were unchanged ester, methyl alcohol, and tetrahydrofuran.

VII. *Synthesis of Authentic cycloPropanealdehyde*.—*cycloPropyl cyanide* (Henry, *Rec. Trav. chim.*, 1899, **18**, 228; Dalle, *ibid.*, 1902, **21**, 123; Demjanov and Fortunatov, *Ber.*, 1907, **40**, 4307; Demjanov and Dojarenko, *Ber.*, 1908, **41**, 43). γ -Chlorobutyronitrile (141 g.) was added slowly to potassium hydroxide pellets (200 g.) contained in a flask immersed in an oil-bath at 190°. The distillate was collected and extracted with ether, the extract dried over potassium carbonate, and distilled, giving 29 g. (33%) of the cyclic cyanide, b. p. 132—134°. During the reaction much ammonia was evolved. The flask residue was dissolved in water and acidified (Congo-red), and the solution repeatedly extracted with ether; distillation gave *cyclopropanecarboxylic acid*, 25 g., b. p. 180—184°.

cycloPropanealdehyde. Stannous chloride was dried by heating in a vacuum to 200° and then suspended in ether (500 c.c.) which had previously been dried over phosphoric oxide and distilled. Hydrogen chloride was then introduced until two layers were formed (cf. Stephen, J., 1925, **127**, 1874). *cycloPropyl cyanide* (27 g.) was added, and the mixture well shaken at intervals during 3 hours. Water was added, the ether removed, and the residue distilled in steam. The distillate consisted of ether, water, unreacted nitrile, and some aldehyde, not isolated, but indicated by preparation of derivatives to be 5.5 g. (20%). The 2:4-dinitrophenylhydrazone separated from ethyl acetate in orange-red prisms, m. p. 168—172° (Found: C, 47.2; H, 4.3; N, 21.3. Calc. for $C_{10}H_{10}O_4N_4$: C, 48.0; H, 4.0; N, 22.4%). The *p*-nitrophenylhydrazone crystallised from ethyl alcohol in golden-brown prisms, m. p. 129—132° (Found: C, 58.7; H, 5.3; N, 20.3. Calc. for $C_{10}H_{11}N_3O_2$: C, 58.5; H, 5.4; N, 20.5%). These two derivatives were used for the mixed m. p.'s already referred to.

VIII. *Methyl Vinyl Ketone*.—Derivatives of this ketone were made for reference purposes. 4-Hydroxybutan-2-one (Wohl and Prill, *Annalen*, 1924, **44**, 139; D.R.-P., 223,207; Friedländer, Vol. 10, p. 1007) was prepared by keeping a mixture of acetone (300 g.), formalin (35%, 100 g.), and sodium hydroxide (0.5N, 10 c.c.) for one hour below 30°. After neutralisation, the liquid was distilled, giving the ketone, 30 g., b. p. 90—100°/17 mm. Repetition of the example described in the patent gave from 1 kg. of acetone, 75 g. of hydroxy-ketone, b. p. 75—100°/17 mm. The acetyl derivative, b. p. 90—100°/17 mm., prepared by reaction with boiling acetic anhydride in presence of zinc chloride, was pyrolysed by passage through a Pyrex tube filled with earthenware rings at 450°. The resulting ketone, b. p. 77—80°, 60% yield, did not give a homogeneous 2:4-dinitrophenylhydrazone or *p*-nitrophenylhydrazone but with phenylhydrazine produced 1-phenyl-3-methylpyrazoline, b. p. 170—180°/17 mm., pale brown prisms, m. p. 71—74°, from ethyl alcohol (Found: C, 74.6; H, 7.2; N, 17.6. Calc. for $C_{10}H_{12}N_2$: C, 75.0; H, 7.6; N, 17.5%). This gave an intense violet coloration with acidified ferric chloride solution. The substance depressed the m. p. of the phenylhydrazone of (II) to 45—55°.

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