

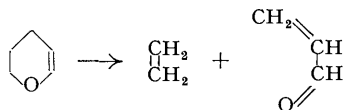
221. *The Thermal Decomposition of 2 : 3-Dihydro- γ -pyran. A New Preparation of Acraldehyde.*

By JOHN G. M. BREMNER, DAVID G. JONES, and STANLEY BEAUMONT.

2 : 3-Dihydro- γ -pyran decomposes at 500—540° to give an 85% yield of acraldehyde and an 88% yield of ethylene. Addition of about 1% of methyl iodide does not increase the rate of formation of acraldehyde, but increases its rate of decomposition.

The yield of acraldehyde is not improved by use of an alumina-silica gel catalyst.
The material of the pyrolysis tube seems unimportant.

This paper describes a new and convenient method for the preparation of acraldehyde. The starting material



is 2 : 3-dihydro- γ -pyran (hereinafter referred to as dihydropyran) which is easily prepared by the dehydration of tetrahydrofurfuryl alcohol (*Org. Synth.*, **23**, 25; B.P. 547,334).

The thermal decomposition of dihydropyran at atmospheric pressure and 500—550° gives acraldehyde and ethylene (Nos. 1 and 2, Table I); some carbon monoxide, hydrogen, and high-boiling residues probably derived from acraldehyde are also formed. In the type of apparatus here described, 500 g. of dihydropyran/l. of reaction space/hr. can be decomposed to give about 300 g. of crude product from which 280 g. of pure acraldehyde can be obtained.

Details from other methods of preparing acraldehyde are given in Table II; advantages of this method are that no catalyst is required and that it can be operated continuously at atmospheric pressure to give excellent yields. The starting material is fairly readily available and is nearly all converted during one passage through the converter. The material of the pyrolysis tube seems to be unimportant as equally good results were obtained using tubes made of "Pyrex" glass, silica, mild steel, or 18/8 chrome-nickel steel.

This decomposition resembles those of the more complex heterocyclic compounds (I) and (II); thus, (I) breaks down when distilled at 11 mm. to give ethylene and furan-3 : 4-dicarboxylic acid (Alder and Reichert, *Ber.*, 1937, **70**, 1354) and (II) gives stilbene and phenanthraquinone when heated to 270° or treated with concentrated sulphuric acid at room temperature (Schönberg and Mustafa, *J.*, 1944, 387). The decomposition also resembles that of cyclohexene and some substituted cyclohexenes to give ethylene and butadiene or a sub-



stituted butadiene (Zelinsky, Mikhailov, and Arbuzov, *J. Gen. Chem. Russia*, 1934, **4**, 856; Rice, Ruoff, and Rodowskas, *J. Amer. Chem. Soc.*, 1938, **60**, 785; Rice and Murphy, *ibid.*, 1944, **66**, 785; Kuchler, *Trans. Faraday Soc.*, 1939, **35**, 874). In contrast with dihydropyran, however, the decomposition of cyclohexene gives ethylene and butadiene in good yield only if carried out at low pressures under conditions in which 60% of the cyclohexene is unchanged. A comparison of the conditions and results of the decompositions of cyclohexene and dihydropyran is given in Table III. It is interesting to note that the heats of reaction calculated from Pauling's bond energy values seem to be low compared with those derived by using other methods.

While the union of ethylene and butadiene to give cyclohexene has been carried out (Joshel and Butz, *J. Amer. Chem. Soc.*, 1941, **63**, 3350), no synthesis of dihydropyran from ethylene and acraldehyde has been reported.

Experiments were also carried out at temperatures in the range 475—550°; the results (Table IV) show a large variation in the proportion of carbon monoxide in the product, apparently independent of the amount of dihydropyran used up.

Many pyrolyses are known to proceed by a free-radical chain mechanism. Accordingly the influence of methyl iodide and of nitric oxide on the rate of production of acraldehyde was examined as methyl iodide is known to catalyse reactions involving free-radical chain mechanisms (Berents and Frost, *Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **24**, 883; *Chem. Abs.*, 1940, 4058), and nitric oxide may have the opposite effect (Staveley and Hinshelwood, *J.*, 1937, 1568). The results of these experiments are given in Table V. In presence of methyl iodide, the total volume of gas produced has increased only slightly, while the proportion of carbon monoxide has increased greatly. This suggests that a reaction, apart from the decomposition of dihydropyran, is being catalysed which does proceed through a free-radical chain mechanism. This reaction is probably the decomposition of acraldehyde, which is known to be catalysed by iodine (Thompson and Frewing, *Trans. Faraday Soc.*, 1935, **31**, 1660), by ethylene oxide (Fletcher and Rollefson, *J. Amer. Chem. Soc.*, 1936, **58**, 2135), and by methyl iodide (Nos. 8 and 9, Table V). Nitric oxide has an effect similar to but less marked than that of methyl iodide. Now, the effect of nitric oxide on thermal decompositions is dependent on the concentration (Staveley and Hinshelwood, *Proc. Roy. Soc.*, 1939, *A*, **159**, 192), and in high concentration the effect may be to increase the rate of decomposition. The concentration of nitric oxide on the acraldehyde formed will naturally be high during the early stage of the reaction so that any inhibiting action may be masked.

The thermal decomposition of acraldehyde is a free-radical reaction propagated by a chain mechanism and it is likely that its rate of decomposition may be greatly affected by the presence of small amounts of impurities, say in the dihydropyran. This may explain the varying amounts of carbon monoxide found in the gaseous products of the decompositions of dihydropyran (Table IV), since under our conditions acraldehyde decomposes to give a gas consisting mostly of carbon monoxide (No. 8, Table V). It is concluded from these

TABLE I.
Results of Thermal and Catalysed Decomposition of Dihydropyran.*

No.	Temp.	Dihydro- pyran fed (g.).	Rate, l. liq./ l. pyrolysis space/hr.	Vol. of exit gas (l.) (S.T.P.) (N-free).	Analysis of exit gas (Orsat)(vol.%)				Liquid and gaseous product (g.)	Liquid product (g.)	Analysis of product (g.).	Dihydro- pyran converted (%).	Yield (%) Acralde- hyde (a) and ethyl- ene (b)
					CO ₂	C _n H _{2n}	CO	H ₂					
1	540°	960	0.6	260	0.4	92.5	7.5	0	0	577	879	100	84.5 (a) 87.5 (b)
2 †	515	140	0.5	36.7	0.3	93.6	4.2	1.5	0.4	90	131.8	97.1	72.5 (a) 88.4 (b)
3 ‡	500	366	0.7	90.0	0.7	91.0	3.2	0.4	4.7	231.5	330.5	81.0	76.5 (a) 96.9 (b)
4 §	405	678	0.7	18.0	Analysis not reliable owing to large pro- portion of nitrogen present.				616 (contain- ing 38 g. water)	616	372	45	4 (a)

* A silica converter tube was packed with glass wool for Run 1, silica chips for Run 2, and with alumina-silica gel catalyst (see Experimental) for Runs 3 and 4.
† A sample of the exit gas distilled in a low-temperature still gave the following results (% by vol.): CO, 5.2; H₂, 0.4; CH₄, 0.5%; C₂H₄, 92.5; C₂H₆, 0.1; C₃, 0.6; C₄, 0.7.

‡ A sample of the exit gas distilled in a low-temperature still showed that 99% of the unsaturated hydrocarbons was ethylene.
§ Poor weight recovery may be due to water retained in the catalyst from a dehydration reaction.

TABLE II.

Methods for Preparing Acraldehyde.

1	Starting material.	Reagent or catalyst.	Temp.	Reaction products.	Yield (%).	Reference.
2	Glycerol	Phosphates of Gp. I	400—420	C ₃ H ₄ O + HCl	75—80	U.S.P. 1,916,743
3	Epichlorohydrin	CaCO ₃	200	C ₃ H ₄ O + H ₂ O	60	U.S.P. 2,106,347
4	Allyl alcohol	Cu	375	C ₃ H ₄ O + H ₂ O	78	F.P. 788,921
5	Allyl ether	Quartz	575	C ₃ H ₄ O + CH ₂ =CH ₂	—	U.S.P. 2,309,576
6	Propylene	HgSO ₄ in H ₂ SO ₄	80	C ₃ H ₄ O + H ₂ O	75% on HgSO ₄	U.S.P. 2,197,258
7	Acetylene + formaldehyde	Metals, salts or oxides	180—300	C ₃ H ₄ O	—	U.S.P. 2,288,335
8 *	Formaldehyde + acetaldehyde	Dehydration catalysts	250—325	C ₃ H ₄ O + H ₂ O	—	U.S.P. 2,245,582
9 *	" "	Inert contact mass	200—600	" "	—	U.S.P. 2,246,037

* According to U.S.P. 2,277,887, it is important to prevent the vapours from the reaction described in Nos. 8 and 9 from coming into contact with Fe or Al; Cu, Ag, Ni, Cr, or ceramic materials may be used.

TABLE III.

Comparisons of Thermal Decompositions of Dihydropyran and cycloHexene.

	Dihydropyran.	cycloHexene. ¹
Moles used	1.0	1.0
Moles decomposed	1.0	0.39
Temperature	540°	790°
Pressure (mm.)	760	10—13
Contact time (secs.)	7.6	0.02
Moles feed/l. total reaction space/hr.	6.6	32.5
Yield (% theory on starting material destroyed) :		
Acraldehyde	84.5	—
Ethylene	87.5	93.0
Butadiene	—	92.2
Hydrogen	—	2.0
Approx. heats of reaction (kg. cal./mole) :		
(a) From heat of combustion ²	—	43.1
(b) From bond energies ³	17	45.5
Pauling ⁴	8.2	31.1
(c) Group substitution method ⁵	17.3	41.9

¹ Details of the pyrolysis from Rice, Ruoff, and Radowskas, *J. Amer. Chem. Soc.*, 1938, **60**, 955.² Heat of formation of butadiene, Rossini, *Chem. Reviews*, 1940, **27**, 1; heat of combustion of cyclohexene, Kharasch, *J. Res. Nat. Bur. Stand.*, 1929, **2**, 359; heat of combustion of ethylene, Kharasch and Knowles, *ibid.*, 1939, **19**, 339.³ No corrections for resonance energies of dihydropyran or acraldehyde as they are about equal (Kistiakowsky, *Chem. Reviews*, 1937, **20**, 181), resonance energy of butadiene taken as 3.5 kg.-cals. (calc. from hydrogenation heats, Kistiakowsky, *loc. cit.*).⁴ "Nature of the Chemical Bond," Pauling, Cornell University Press, 1944; assumptions of resonance energies in Ref. 3.⁵ Anderson, Beyer, and Watson, *Nat. Petroleum News*, 1944, **36**, R, 476.

TABLE IV.

Variation of Carbon Monoxide in Product in Thermal Decomposition of Dihydropyran.

(Pyrolysis carried out in silica tube packed with silica chips.)

Temp.	Space velocity, l. liquid/l. pyrolysis space/hr.	Analysis of exit gas after condensing system, % by vol. (Orsat).				Dihydropyran converted (%).
		CO ₂ .	C _n H _{2n} .	CO.	H ₂ .	
475°	1.6	0.7	90.0	9.0	0.3	12.0
490	0.56	0.0	94.0	3.7	2.3	50.0
495	1.1	1.0	82.5	15.5	1.0	41.8
500	0.6	0.8	87.5	11.3	0.4	48.5
505	2.8	0.0	95.8	3.9	0.3	17.1
515	0.5	0.0	92.5	5.2	0.4	97
540	0.6	0.4	92.5	7.5	0	100

TABLE V.

Effect of Methyl Iodide and Nitric Oxide on the Pyrolysis of Dihydropyran and Acraldehyde.

(Pyrolysis carried out in a silica tube packed with silica chips as described in Experimental section. Temperature, 450°. Space velocity, 0.5 l. liquid/l. pyrolysis space/hr.)

No.	Feed.	Added material.	Moles gas/mole feed.				Moles C _n H _{2n} Moles CO
			H ₂ .	C _n H _{2n} .	CO.	Total.	
1	Dihydropyran	None	0.007	0.19	0.007	0.20	27.2
2	"	"	0.004	0.29	0.013	0.30	22.4
3	"	1% CH ₃ I	—	0.27	0.047	0.32	5.7
4	"	"	0.001	0.20	0.030	0.23	6.6
5	"	"	0.002	0.27	0.070	0.34	3.8
6	"	0.3% NO	0.010	0.22	0.014	0.24	15.7
7	"	0.4% NO	0.002	0.23	0.023	0.25	10.0
8	Acraldehyde	None	—	—	—	0.01	—
9	"	1% CH ₃ I	0.003	0.001	0.02	0.02	0.06

results that the thermal decomposition of dihydropyran does not take place to any extent through a chain mechanism involving free radicals.

The use of alumina-silica gel catalysts in the "cracking" of petroleum hydrocarbons has received considerable attention. Its effect may be to change completely the course of the reaction compared with the uncatalysed, thermal decomposition; thus, cyclohexene passed over such a catalyst at 300° and at atmospheric pressure gave a 70% yield of methyl cyclopentenenes (Bloch and Thomas, *J. Amer. Chem. Soc.*, 1944, **66**, 1589; cf. also Greensfelder and Voge, *Ind. Eng. Chem.*, 1945, **37**, 983). The results (Nos. 2 and 3, Table I) show that an alumina-silica gel catalyst had no effect in changing the course of the thermal decomposition of dihydropyran at 500°; at 400°, unidentified high-boiling products were formed. Some of the work described in this paper has formed the subject matter of B.P. 573,507.

EXPERIMENTAL.

The pyrolysis tube (110 cm. \times 2 cm. i.d.) was contained in a vertical iron tube electrically heated by means of three separately controlled electrical windings. The temperatures in the annulus between the pyrolysis tube and the furnace wall were measured by two fixed thermocouples, while the temperatures inside the tube were measured by means of a moveable thermocouple in a glass or silica sheath passing down the axis of the tube. The volume of empty pyrolysis zone was 100 ml.; when packed with silica chips the free space was 53 ml. Dihydropyran was run into the top of the pyrolysis tube through a capillary tube; the rate was controlled by varying the pressure of nitrogen on a calibrated reservoir. The products were cooled by a water-cooled double surface condenser and the condensate caught in an ice-cooled catchpot containing some quinol to stabilise the acraldehyde. Uncondensed material then passed through a catchpot cooled in solid carbon dioxide-methanol and then through a rotary gas meter to the atmosphere. When only a small volume of gas was evolved, all the gas was collected in a large aspirator over acidified brine.

The decompositions were carried out in the following tubes: (1) silica tube packed with silica chips; (2) "Pyrex" glass tube packed with "Pyrex" glass cuts or glasswool; (3) "Pyrex" glass tube packed with 18/8 Cr-Ni steel turnings; (4) mild steel tube (unpacked); (5) 18/8 Cr-Ni steel tube packed with turnings of the same material; (6) silica tube packed with 100 ml. of alumina-silica gel catalyst.

Materials.—Tetrahydrofurfuryl alcohol was dehydrated to dihydropyran by the method described in B.P. 547,334. Acraldehyde was prepared from dihydropyran as described in this paper; it was stabilised with 0.1% of quinol and was redistilled before use. Nitric oxide was prepared from ferrous sulphate and sodium nitrite solution (Weil-Malherbe and Weiss, *J.*, 1944, 541); it was washed with 20% sodium hydroxide solution before use and was passed into the apparatus from a gas burette through a tube containing pellets of sodium hydroxide. Alumina-silica gel catalyst was prepared according to the method given in U.S.P. 2,270,090.

Analysis of Products.—The reaction products condensed in the catchpots were analysed by distillation at atmospheric pressure through a 3-inch column estimated to contain 6–7 theoretical plates. The uncondensed gas was analysed in an "Orsat" apparatus, and the gaseous products from two runs (Nos. 1 and 2, Table V) were analysed by distillation in a low-temperature still.

Properties of Acraldehyde from Thermal Decomposition (No. 1, Table I).—The properties of the twice distilled acraldehyde are compared in Table VI with the literature and calculated values.

TABLE VI.

Properties of Acraldehyde obtained by Thermal Decomposition.

Source.	B. p.	d_4^{20} .	n_D^{20} .	C (%)	H (%)	CHO (%)*
Thermal decomp.	52–54°	0.837	1.4025	64.2	7.2	52.5
Lit. or calc. for C_3H_4O	52.5	0.841	1.3997	64.3	7.1	51.78

* The analysis was done by Ripper's method, using potassium hydrogen sulphite ("Volumetric Analysis," Sutton, 1935, 12th Edn.); high results were obtained with the same sample using the method of oximation under pressure in presence of pyridine (59.5%, 60.4% CHO) (Smith and Bryant, *J. Amer. Chem. Soc.*, 1935, 57, 57) or the normal sulphite method (61.0%, 61.6% CHO).

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