26. *Stereochemical Studies of Olefinic Compounds. Part V.* Further Observations on the Ring Fission of* 3-*Chlorotetrahydro-furans and -pyrans.*

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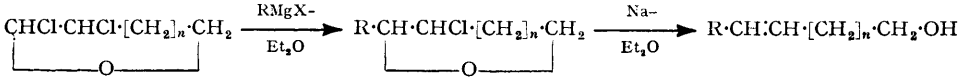
Chlorination of tetrahydrofuran and tetrahydropyran yields *trans*-2 : 3-dichlorotetrahydrofuran and *trans*-2 : 3-dichlorotetrahydropyran, identical with the compounds obained by adding chlorine to 2 : 3-dihydrofuran and 3 : 4-dihydropyran respectively. The configurations assigned to the two stereoisomers of the 2-alkyl-3-chlorotetrahydrofurans on the basis of the Auwers–Skita rules are supported by comparison of their speeds of dehydrochlorination with sodium ethoxide. Quantitative infrared analyses of the *cis-trans* mixtures of pent-3-en-1-ols and hex-3-en-1-ols formed on sodium ring fission of *cis*- and *trans*-3-chloro-2-methyl- and -ethyl-tetrahydrofurans are reported.

Some reactions of 3-chlorotetrahydro-furans and -pyrans are reported.

Fission of β-halogeno-ethers with electropositive metals is a valuable general reaction for the introduction of an olefinic linkage and many aspects of this reaction have now been examined. We have been especially interested in it as a method for chain extension by schemes outlined in Parts II and III (Crombie and Harper, *J.*, 1950, 1707, 1714). These involve treating an alkylmagnesium halide with 2 : 3-dichlorotetrahydro-furan or -pyran (I, $n = 1$ or 2) and ring fission of the 2-alkyl-3-chloro-intermediate (II) with sodium to give an alk-3-en-1-ol or an alk-4-en-1-ol (III; $n = 1$ or 2). The present contribution is concerned with both the intermediates and the fission products.



$$\underbrace{\text{CHCl·CHCl·[CH}_2]_n\text{·CH}_2}_{\text{O}} \xrightarrow[\text{Et}_2\text{O}]{\text{RMgX-}} \underbrace{\text{R·CH·CHCl·[CH}_2]_n\text{·CH}_2}_{\text{O}} \xrightarrow[\text{Et}_2\text{O}]{\text{Na-}} \text{R·CH:CH·[CH}_2]_n\text{·CH}_2\text{·OH}$$

(I) (II) (III)

The starting materials for chain extension by four or five carbon atoms are normally the dichloro-compounds (I; $n = 1$ or 2), though for the latter Brandon, Derfer, and Boord (*J. Amer. Chem. Soc.*, 1950, **72**, 2120) have used 2 : 3-dibromotetrahydropyran. However, this gives less stable products and inferior yields (cf. Parham and Holmquist, *ibid.*, 1954, **76**, 1173). 2 : 3-Dichlorotetrahydropyran is best prepared by addition of chlorine to 3 : 4-dihydropyran and this type of addition is generally recognised as *trans* (Barton and Miller, *ibid.*, 1950, **72**, 1067; references cited by Crombie and Harper, *J.*, 1950, 1714). On the other hand 2 : 3-dichlorotetrahydrofuran is best prepared by chlorination of tetrahydrofuran in presence of an iodine catalyst. Its geometrical configuration has been unknown. Both dichloro-compounds are homogeneous, as judged by their behaviour on distillation. We have now prepared 2 : 3-dichlorotetrahydropyran by chlorination of tetrahydropyran under conditions which correspond to those used for the chlorination of tetrahydrofuran and, correspondingly, 2 : 3-dichlorotetrahydrofuran by addition of chlorine to dihydrofuran. Infrared absorption spectra show the two dichlorotetrahydrofurans and the two dichlorotetrahydropyrans to be severally identical, thus demonstrating that the chlorination (substitution), whatever its mechanism, yields a *trans*-product. Samples of dihydrofuran for this work were originally prepared by β-halogeno-ether cleavage from 3-chloro-2-ethoxytetrahydrofuran (Normant, *Compt. rend.*, 1949, **228**, 102); of the two ether linkages present the exocyclic one is ruptured at a greater speed than the cyclic one. However, it was difficult to obtain the dihydrofuran pure enough, so eventually the material was prepared by Paul, Fluchaire, and Collardeau's isomerisation method (*Bull. Soc. chim. France*, 1950, 668).

2 : 3-Dichlorotetrahydrofuran with methyl-, ethyl-, *iso*propyl-, and *tert.*-butylmagnesium halides yielded the four corresponding 2-alkyl-3-chlorotetrahydrofurans and these were fractionally distilled to give specimens of the *cis*- and *trans*-isomers of the first

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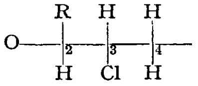
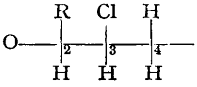
* Part IV, *J.*, 1955, 1512.

three compounds. (The *tert.*-butyl isomers decomposed rapidly on distillation and fractionation was impossible.) Although specimens of the three pairs of isomers were obtained, resolution of the mixtures was not complete with the helices-packed column employed. Nevertheless it was possible to estimate, by refractometric analysis of the intermediate fractions, that the 3-chlorotetrahydro-2-methylfuran and 3-chloro-2-ethyltetrahydrofuran contained approximately 35% of the lower-boiling *trans*-isomer, whilst the 3-chloro-2-*iso*propyltetrahydrofuran contained about 50% of the *trans*-isomer. Inversion at $C_{(2)}$ is thus somewhat reduced with the larger incoming alkyl group.

Assignment of configurations to the above compounds is based upon the Auwers–Skita rules which are likely to be valid in this and the corresponding 2-alkyl-3-chlorotetrahydropyran series (for information on the scope of the rules, see Haggis and Owen, *J.*, 1953, 408). Substantiation comes from the rates of dehydrochlorination of the three pairs of isomers (II; $n = 1$, R = Me, Et, and Pr^i) with ethanolic sodium ethoxide. The three lower-boiling isomers reacted at almost the same speed whereas the three higher-boiling isomers reacted considerably faster, the rate increasing in the order $\text{Pr}^i < \text{Et} < \text{Me}$. In the *trans*-isomer, a *trans*-elimination of hydrogen chloride is possible only between $C_{(3)}$ and $C_{(4)}$, whereas in the *cis*-isomer a similar *trans*-elimination is possible between $C_{(3)}$ and $C_{(2)}$ as well as between $C_{(3)}$ and $C_{(4)}$, and it can be deduced from Normant's results (*Compt. rend.*, 1948, **227**, 283) that a hydrogen atom at $C_{(2)}$ is more reactive than one at $C_{(4)}$.


trans


cis

If it is conceded that *trans*-elimination is highly probable in this reaction and in a system of this type, these experiments reinforce the assignments of configuration made above. It is of interest that Riobé [*Ann. Chim.* (*France*), 1949, **4**, 593] has shown that in parallel eliminations in the 2-alkyl-3-chlorotetrahydropyran series the lower-boiling isomers (II; $n = 2$, R = Et, Pr^n, and Bu^n) react at the same speed, whilst that with R = Me is rather slower. All four higher-boiling isomers react faster than any of the lower-boiling ones and in the order $\text{Bu}^n = \text{Pr}^n < \text{Et} < \text{Me}$.

It was found qualitatively (Crombie and Harper, *loc. cit.*) that, whereas both *cis*- and *trans*-2-alkyl-3-chlorotetrahydropyrans yield *trans*-alk-4-en-1-ols when treated with sodium metal, *cis*-2-alkyl-3-chlorotetrahydrofurans give a mixture of comparable proportions of *cis*- and *trans*-alk-3-en-1-ols. *trans*-3-Chloro-2-methyltetrahydrofuran gave largely *trans*-pent-3-en-1-ol, though it was evident from both spectroscopic and chemical evidence that a little *cis*-pent-3-en-1-ol was present. Quantitative investigation of the composition of the pent-3-en-1-ols and hex-3-en-1-ols formed on ring scission of the 3-chlorotetrahydro-2-methyl- and 3-chloro-2-ethyltetrahydro-furans has now been made by an infrared spectroscopic technique described in the Experimental Section. The results are summarised in the Table. They are in agreement with our qualitative results except that the amounts of *cis*-alcohol produced on fission of the *trans*-2-alkyl-3-chlorotetrahydrofurans are rather larger than we had suspected. Samples of the alcohols prepared earlier were also examined and the results agreed very well with those in the Table.

2-Alkyl-3-chlorotetrahydrofuran	Product		
cis-2-Methyl	43% *cis*-	57%	*trans*-pent-3-en-1-ol
cis-2-Ethyl	44	56	hex-3-en-1-ol
trans-2-Methyl	13	87	pent-3-en-1-ol
trans-2-Ethyl	20	80	hex-3-en-1-ol

The infrared absorption spectra of *cis*- and *trans*-pairs of 2-alkyl-3-chlorotetrahydrofurans and -pyrans have been determined and in each case confirm the differing identities of the isomers. However, although it is clear that no *cis*-isomer is present in the *trans*-isomer (and *vice versa*) in the case of 3-chloro-2-methyltetrahydropyran, yet with 3-chlorotetrahydro-2-methyl- and 3-chloro-2-ethyl-tetrahydrofurans the spectra do not contain suitable bands to enable this possibilty to be excluded altogether. Were the lower-boiling fractions azeotropes, the concentration of *cis*-isomers needed to account for the *cis*-alkenols produced on fission of the *trans*-isomers would have to be considerable.

During the present work a number of observations of preparative interest were made. For routine large-scale preparations of alkenols a technique is described in the Experimental section whereby a 2-alkyl-3-chlorotetrahydro-furan or -pyran is prepared in the usual way by using an excess of Grignard reagent, and then transferred under nitrogen slowly into a flask containing sodium under ether. This avoids isolation of the pure intermediate and the yield of *trans*-hex-4-en-1-ol has been raised from 50 to 75% overall by this procedure. It was mentioned above that 2-*tert*.-butyl-3-chlorotetrahydrofuran decomposes readily and Brandon *et al.* (*loc. cit.*) record that *tert*.-butylmagnesium bromide fails to react with 2 : 3-dibromotetrahydropyran. With 2 : 3-dichlorotetrahydropyran reaction clearly takes place but we have not succeeded in isolating a product or in subjecting it to ring fission under the above conditions. A small quantity of 2-*tert*.-butyl-3-chlorotetrahydrofuran has been isolated and with sodium gave an alcohol having the correct analysis for 5 : 5-dimethylhex-3-en-1-ol.

The feasibility of two successive chain extensions by five carbon atoms was examined by using *n*-butyl bromide and dihydropyran as starting points. These were converted into non-4-en-1-ol in the usual way. Conversion into the bromide followed by a second chain extension gave *n*-tetradeca-4 : 9-dien-1-ol, presumed to be the *trans-trans*-form from its mode of formation. The overall yield was 12% based on the first batch of dihydropyran. Ring fission becomes more sluggish as longer alkyl or alkenyl residues are employed and the yield from the second reaction was 66%, against 84% for the first. The *n*-tetradeca-4 : 9-dien-1-ol was catalytically hydrogenated to tetradecanol, and this oxidised to tetradecanoic acid to confirm its identity.

Though the 2-alkyl-3-chlorotetrahydro-furans and -pyrans are readily prepared by the methods mentioned above, the first members of the series, 3-chlorotetrahydro-furan and -pyran have hitherto been much less accessible [cf. Ou Kiun-Houo, *Ann. Chim.* (*France*), 1940, **13**, 175; Colonge and Garnier, *Bull. Soc. chim. France*, 1948, 434; Paul, *Angew. Chem.*, 1951, **63**, 301]. We now find that they are readily prepared by treatment of the 2 : 3-dichloro-compounds with lithium aluminium hydride in ether. Ring fission of the products with sodium gives but-3-en-1-ol and pent-4-en-1-ol in good yield. Pent-4-en-1-ol is more readily prepared by ring fission of tetrahydrofurfuryl chloride but this preparation of but-3-en-1-ol is convenient for small-scale work. Treatment of 2-chloromethyltetrahydropyran with sodium yields hex-5-en-1-ol in 86% yield and Eglington, Jones, and Whiting (*J.*, 1952, 2873) have shown that with sodamide it yields hex-5-yn-1-ol (80%). These authors report difficulty in the preparation of acraldehyde dimer and 2-hydroxymethyltetrahydropyran required as intermediates. Both stages proved satisfactory under the conditions used by us and higher yields of chloride were also obtained.

Eglington, Jones, and Whiting (*loc. cit.*) report that 3-chloro-2-ethyltetrahydrofuran gives only a 30% yield of hex-3-yn-1-ol when treated with sodamide. We have also obtained only poor yields of alk-3-yn-1-ols when 3-chloro-2-methyl-, -ethyl-, and -*iso*propyltetrahydrofurans are stirred with sodamide in liquid ammonia (28, 20, and 17% respectively). 3-Chlorotetrahydropyran gives a 20% yield of pent-4-yn-1-ol. In all cases low-boiling elimination products are formed and the method is of limited preparative interest.

2 : 3-Dichlorotetrahydropyran reacts with the nucleophilic reagent ethyl sodiomalonate to give 3-chloro-2-(diethoxycarbonylmethyl)tetrahydropyran, though the yield is poor and much low-boiling material is formed by solvolysis or perhaps elimination.

EXPERIMENTAL

Infrared absorptions were determined with a Grubb-Parsons single-beam spectrometer coupled to a Brown recorder, the pure liquids being used as capillary films.

2 : 3-*Dichlorotetrahydropyran from Tetrahydropyran*.—Dry chlorine was passed into tetrahydropyran (30 g.) in carbon tetrachloride (30 ml.) containing iodine (0·2 g.) under the conditions described for tetrahydrofuran (Part III, *J.*, 1950, 1714). Working up under similar conditions gave *trans*-2 : 3-dichlorotetrahydropyran (34 g., 63%), b. p. 86—90°/20 mm., n_D^{20} 1·4945 (Found : C, 38·7 ; H, 5·3; Cl, 45·65. Calc. for $C_5H_8OCl_2$: C, 38·75; H, 5·2; Cl, 45·75%). A specimen

prepared by addition of chlorine to dihydropyran (cf. Part II, *J.*, 1950, 1707) had b. p. 88—90°/20 mm., n_D^{20} 1·4946. The infrared spectra of the two compounds were identical (29 bands) in the region 700—3300 cm.$^{-1}$.

2 : 3-*Dichlorotetrahydrofuran from Dihydrofuran.*—2 : 3-Dihydrofuran (10 g.; prepared by the isomerisation method from 2 : 5-dihydrofuran) was treated in dry ether (75 ml.) with dry chlorine until a faint green tint persisted. The colour was discharged with a few drops of dihydrofuran, the ether evaporated, and the residue distilled, to give *trans*-2 : 3-dichlorotetrahydrofuran (16·1 g., 80%), b. p. 65—70°/22 mm., n_D^{20} 1·4840 (Found : Cl, 50·1. Calc. for $C_4H_6OCl_2$: Cl, 50·3%). A specimen prepared by chlorination of tetrahydrofuran (cf. Part III) had b. p. 63—66°/21 mm., n_D^{20} 1·4841. The infrared spectra of the two compounds were identical in the region 800—3300 cm.$^{-1}$.

2 : 3-Dichlorotetrahydrofuran prepared from the dihydrofuran described below had b. p. 66—72°/23 mm., n_D^{20} 1·4810 (Found : C, 34·1; H, 4·1; Cl, 49·7. Calc. for $C_4H_6OCl_2$, : C, 34·1; H, 4·1%). Its infrared spectrum differed from those above only in relative intensities at 1030 and 1061 cm.$^{-1}$.

2-*Alkyl*-3-*chlorotetrahydrofurans.*—These were prepared according to the procedure of Part III, the yields of mixed isomers being methyl, 83, ethyl, 87, and *iso*propyl, 57%. Each was fractionally distilled through a 120 × 2·5-cm. glass helices-packed column with a total-reflux variable take-off. Resolution of the mixtures was not complete and the content of *cis*- and *trans*-isomers in intervening fractions was estimated refractometrically. The physical properties of the best fractions were as shown. For the methyl, ethyl, and *iso*propyl compounds the calculated molecular refractivities are 29·60, 34·22, and 38·84 respectively. For previous physical data on the methyl and ethyl stereoisomers see Part III. trans- (Found : C, 56·15; H, 8·6; Cl, 23·5. $C_7H_{13}OCl$ requires C, 56·55; H, 8·8; Cl, 23·85%), and cis-3-*Chlorotetrahydro*-2-iso*propylfuran* (Found : C, 56·4; H, 8·6; Cl, 23·5%) are new.

2-Methyl, *trans* :	b. p. 130°,	n_D^{19} 1·4424,	d_4^{19} 1·078,	$[R_L]_D$ 29·60
,, *cis* :	147	1·4532	1·104	29·54
2-Ethyl, *trans* :	150	1·4459	1·046	34·32
,, *cis* :	165	1·4556	1·075	34·02
2-*iso*Propyl, *trans* :	164	1·4482	1·027	38·77
,, *cis* :	178	1·4568	1·053	38·44

Ring Fission of the Stereoisomeric 2-*Alkyl*-3-*chlorotetrahydrofurans by Sodium.*—The *trans*-2-methyl compound gave α-pent-3-en-1-ol (64%), b. p. 136—137°, n_D^{20} 1·4342, and the *cis*-isomer gave β-pent-3-en-1-ol (70%), b. p. 137—138°, n_D^{20} 1·4357. The *trans*-2-ethyl compound gave α-hex-3-en-1-ol (59%), b. p. 63—64°/16 mm., n_D^{20} 1·4383, and the *cis*-isomer gave β-hex-3-en-1-ol (84%), b. p. 64—65°/16 mm., n_D^{20} 1·4393. The *trans*-2-*iso*propyl compound gave α-5-*methylhex*-3-*en*-1-*ol* (86%), b. p. 71—73°/15 mm., n_D^{20} 1·4372 (Found : C, 73·55; H, 12·3. $C_7H_{14}O$ requires C, 73·6; H, 12·35%), and the *cis*-isomer gave β-5-*methylhex*-3-*en*-1-*ol* (70%), b. p. 70—74°/16 mm., n_D^{20} 1·4335 (Found : C, 73·55; H, 12·4%).

For the experimental technique and comparative data on the pent-3-en-1-ols and hex-3-en-1-ols see Part III. The stereochemistry of the α- and the β-5-methylhex-3-en-1-ol has not been further investigated. They are probably mixtures of stereoisomers although the α-form gave a 1-*naphthylurethane*, m. p. 56° (Found : C, 76·2; H, 7·4; N, 4·8. $C_{18}H_{21}O_2N$ requires C, 76·3; H, 7·5; N, 4·9%), and the β-form a 1-*naphthylurethane*, m. p. 63° (Found : C, 76·2; H, 7·6; N, 4·8%). Both these were crystallised from light petroleum (b. p. 60—80°).

Infrared Analysis of the Stereoisomeric Pent-3-*en*-1-*ols and Hex*-3-*en*-1-*ols.*—The pure reference compounds, *trans*-pent-3-en-1-ol and *trans*-hex-3-en-1-ol, were prepared by stereospecific reduction of the corresponding acetylenes with sodium in liquid ammonia (Part I, *J.*, 1950, 873; Sondheimer, *J.*, 1950, 878). *cis*-Pent-3-en-1-ol was a carefully fractionated specimen obtained by semihydrogenation of pent-3-yn-1-ol over palladised calcium carbonate. The infrared spectrum indicated that contamination with *trans*-isomer was very small : none could be detected chemically. Nevertheless, the figures for *cis*-content obtained in the pentenol analyses may be slightly low (1—2%) for this reason. *cis*-Hex-3-en-1-ol was a carefully purified specimen isolated from Brazilian *Mentha arvensis* oil (" leaf alcohol," cf. Parts I and IV).

For analysis, use was made of the facts that the *trans*-alcohols show strong absorption at 967 cm.$^{-1}$, which is almost non-existent in the *cis*-alcohols, whilst both show a strong band at 1040 cm.$^{-1}$ due to the hydroxyl group. The hydroxyl and the *trans*-band are of comparable intensity. This allows analysis to be carried out on liquid films without accurate control of the film thickness. The optical density of the hydroxyl band was usually about 0·4. If $a = d_{967}/d_{1040}$ for the pure *cis*-isomer, $b = d_{967}/d_{1040}$ for the pure *trans*-isomer, and $c = d_{967}/d_{1040}$

for the *cis-trans*-mixture, where d is the optical density, then % *trans*-isomer in the mixture $= 100(c - a)/(b - a)$. The validity of the method was confirmed for four mixtures of the stereoisomeric hex-3-en-1-ols (Weighed: 28, 35, 55, and 76% of *trans*-isomer. Found: 29, 35, 55, and 75% respectively) and for three mixtures of the stereoisomeric pent-3-en-1-ols (Weighed: 62, 74, and 95% of *trans*-isomer. Found: 62, 74, and 95% respectively).

Rates of Reaction of Sodium Ethoxide with cis- *and* trans-*2-Alkyl-3-chlorotetrahydrofurans.*—For each *cis*- and each *trans*-isomer of the 2-alkyl-3-chlorotetrahydrofurans four identical solutions were prepared and sealed in glass ampoules. These consisted of 0·1M-2-alkyl-3-chlorotetrahydrofuran in dry ethanol (10 ml.) mixed with sodium ethoxide solution (20 ml.) [made by dissolving sodium (16 g.) in dry ethanol and making the volume up to 500 ml.]. The ampoules were immersed in a water-bath at 100° for the times stated, then broken into ice-water and acidified with dilute nitric acid, and the liberated chloride ion was titrated by Volhard's method. The results are summarised in the Table.

	Reaction (%) after			
2-Alkyl-3-chlorotetrahydrofuran	20	54	84	120 min.
trans-2-Methyl	7·9	21·0	32·0	45·3
cis-2-Methyl	16·0	41·9	57·0	72·1
trans-2-Ethyl	8·9	20·6	32·6	45·5
cis-2-Ethyl	12·1	32·0	45·1	58·5
trans-2-*iso*Propyl	8·0	21·1	33·0	46·0
cis-2-*iso*Propyl	10·7	29·1	44·0	57·0

For an investigation of the products of dehydrochlorination of 2-alkyl-3-chlorotetrahydrofurans, see Normant, *Compt. rend.*, 1948, **227**, 283.

2-tert.-*Butyl-3-chlorotetrahydrofuran.*—A Grignard reagent was prepared from *tert.*-butyl bromide (300 g., prepared by the method of Bryce-Smith and Howlett, *J.*, 1951, 1141) and magnesium (55 g.) in ether. The reagent was cooled in ice-water, and 2 : 3-dichlorotetrahydrofuran (210 g.) added dropwise. Working up in the usual way gave crude 2-tert.-*butyl-3-chlorotetrahydrofuran* (153 g., 63%), b. p. 80—105°/19 mm. Attempted fractional distillation under reduced pressure caused rapid tar formation and decomposition. Six fractions were recovered from the residue by rapid distillation at 5 mm. Fraction (ii) had b. p. 61—64°/5 mm., n_D^{20} 1·4640 (Found: C, 58·9; H, 9·15; Cl, 21·0. $C_8H_{15}OCl$ requires C, 59·05; H, 9·3; Cl, 21·8%). Fraction (v) had b. p. 75—80°/5 mm., n_D^{20} 1·4652 (Found: C, 58·95; H, 9·15; Cl, 21·2%).

5 : 5-*Dimethylhex-3-en-1-ol.*—2-*tert.*-Butyl-3-chlorotetrahydrofuran (4·8 g.; mixed stereoisomers) was treated with sodium (1·5 g.) under ether (50 ml.), to give 5 : 5-*dimethylhex-3-en-1-ol* (2·3 g., 61%), b. p. 80—81°/16 mm., n_D^{20} 1·4470 (Found: C, 74·9; H, 12·4. $C_8H_{16}O$ requires C, 74·95; H, 12·6%).

trans-*Non-4-enyl Bromide.*—*trans*-Non-4-en-1-ol (156 g.; prepared as described in Part II) was converted by the procedure of Part III into trans-*non-4-enyl bromide* (139 g., 62%), b. p. 83—85°/22 mm., n_D^{20} 1·4690 (Found: C, 53·2; H, 8·45; Br, 38·7. $C_9H_{17}Br$ requires C, 52·7; H, 8·35; Br, 38·95%).

trans-trans-*Tetradeca-4 : 9-dien-1-ol.*—A Grignard reagent was prepared from magnesium (16 g., 0·66 mole) and *trans*-non-4-enyl bromide (135 g., 0·66 mole) in ether (150 ml.) and allowed to react with 2 : 3-dichlorotetrahydropyran (from dihydropyran, 0·5 mole) in the usual way. Working up gave *3-chlorotetrahydro-2-*trans-*non-4′-enylpyran* (81 g., 51% calc. on the bromide), b. p. 130—150°/0·3 mm. (mixture of isomers). Ring fission of the pyran (80 g.) with sodium (17 g.) in ether (140 ml.) gave trans-trans-*tetradeca-4 : 9-dien-1-ol* (45·5 g., 66%), b. p. 139—141°/5 mm., n_D^{20} 1·4590 (Found: C, 79·35; H, 12·25. $C_{14}H_{26}O$ requires C, 79·5; H, 12·45%). The alcohol was hydrogenated over Raney nickel to myristyl alcohol, b. p. 165—168°/15 mm., m. p. 38° (Found: C, 78·3; H, 14·3. Calc. for $C_{14}H_{30}O$: C, 78·5; H, 14·1%). When oxidised with a slight excess of potassium permanganate in 20% sulphuric acid, the myristyl alcohol gave myristic acid, b. p. 121—122°/1 mm., m. p. 57° (Found: C, 73·9; H, 12·1. Calc. for $C_{14}H_{28}O_2$: C, 73·6; H, 12·4%) (lit., b. p. 122°/1 mm., m. p. 58°).

Preparation of Alk-4-en-1-ols without Isolation of the 2-Alkyl-3-chlorotetrahydropyran.—The appropriate Grignard reagent (1·2 mol.) was prepared in a three-necked round-bottomed flask (1 l.) equipped with reflux condenser, stirrer, and dropping funnel. 2 : 3-Dichlorotetrahydropyran was added in the usual way. The stirrer and reflux condenser were then transferred to a second similar flask, containing powdered sodium (2 g.-atoms) under ether, and replaced by a rubber bung and a connection to a nitrogen cylinder. In place of the dropping funnel a glass bridge (8 mm. bore) equipped with rubber bungs was inserted so that it reached the bottom of the flask. The other end was inserted in the flask containing the sodium so that it was well above the surface of the ether. By adjustment of the nitrogen pressure the contents of the first flask were delivered dropwise into the second (4—5 hr.) and any remaining material was washed in with a little ether. Care must be taken in starting the sodium ring fission as initiation seems to be retarded by the excess of Grignard reagent. The product was worked up in the usual manner.

3-*Chlorotetrahydropyran.*—2 : 3-Dichlorotetrahydropyran (160 g.) in anhydrous ether (350 ml.) was treated with a suspension of lithium aluminium hydride (10 g.) in ether (400 ml.) so that gentle refluxing was maintained, then heated under reflux for 40 min. The excess of reagent was decomposed with wet ether and then dilute sulphuric acid. The ethereal layer was dried, the solvent removed under a column, and the residue distilled. The fraction, b. p. 137—146°, was collected (70 g., 56%; n_D^{20} 1·4626), and when redistilled 3-*chlorotetrahydropyran* had b. p. 52—54°/13 mm., n_D^{20} 1·4620 (Found : C, 50·0; H, 7·6; Cl, 30·0. C_5H_9OCl requires C, 49·8; H, 7·5; Cl, 29·4%). An experiment on one-tenth of the above scale gave a yield of 73% (b. p. 140—143°, n_D^{15} 1·4652).

3-*Chlorotetrahydrofuran.*—2 : 3-Dichlorotetrahydrofuran (30 g.) in ether (70 ml.) was treated with lithium aluminium hydride (2 g.) in ether as described above. 3-*Chlorotetrahydrofuran* (15 g., 67%), b. p. 59—61°/30 mm., n_D^{20} 1·4532, was isolated (Found : C, 45·1; H, 6·55; Cl, 33·3. Calc. for C_4H_7OCl : C, 45·05; H, 6·6; Cl, 33·25%).

Pent-4-*en*-1-*ol.*—3-Chlorotetrahydropyran (8·5 g.) in ether (30 ml.) was added slowly to sodium (4 g.) under dry ether (15 ml.). Working up gave pent-4-en-1-ol (4·4 g., 73%), b. p. 134—137°, n_D^{20} 1·4301. The 1-naphthylurethane had m. p. 62°. Robinson and Smith (*J.*, 1936, 195) give b. p. 135—137°, n_D^{20} 1·4312. For the 1-naphthylurethane, Schniepp and Geller (*J. Amer. Chem. Soc.*, 1945, **67**, 54) give m. p. 61·5—62°.

But-3-*en*-1-*ol.*—3-Chlorotetrahydrofuran (10 g.) was added dropwise to sodium (5 g.) under ether (10 ml.), the volume being made up to 50 ml. when reaction had started. But-3-en-1-ol (5·4 g., 79%) had b. p. 111—114°, n_D^{20} 1·4218. Its 1-naphthylurethane, crystallised from light petroleum (b. p. 60—80°), had m. p. 77° (Found : C, 74·5; H, 6·2. Calc. for $C_{15}H_{15}O_2N$: C, 74·7; H, 6·3%). Birch and McAllan (*J.*, 1951, 2556) give b. p. 113·5°/760 mm., n_D^{20} 1·4200. Roberts and Mazur (*J. Amer. Chem. Soc.*, 1951, **73**, 2509) give m. p. 75·2—75·6° for the 1-naphthylurethane.

Reaction of 3-*Chlorotetrahydro-furans and -pyrans with Sodamide and Liquid Ammonia.*—Typical conditions were as follows : Sodamide was prepared in liquid ammonia (500 ml.) from sodium (26 g.) in the presence of ferric nitrate. 3-Chlorotetrahydropyran (34·4 g.) was added dropwise with vigorous stirring which was continued for 6 hr. and then overnight in the presence of anhydrous ether (200 ml.). Next day ammonia solution (*d* 0·88) was added and the ethereal layer separated. The aqueous phase was extracted with ether, and the ethereal extracts were united, dried (Na_2SO_4), and distilled. Two main fractions were obtained : (i) b. p. 85—88°, n_D^{20} 1·4406 (12·4 g., 52%) (Found : C, 71·0; H, 9·4. Calc. for C_5H_8O : C, 71·4; H, 9·6%) (lit. for dihydropyran, b. p. 85°, n_D^{20} 1·4405); (ii) b. p. 150—155°, n_D^{20} 1·4488 (4·9 g., 20%). The 1-naphthylurethane from fraction (ii) had m. p. 83° (Found : C, 75·75; H, 5·85. Calc. for $C_{16}H_{15}O_2N$: C, 75·9; H, 5·95%), undepressed by the authentic 1-naphthylurethane of pent-4-yn-1-ol. Paul and Tchelitcheff (*Compt. rend.*, 1950, **230**, 1473) give b. p. 154—155°, n_D^{19} 1·4432, for pent-4-yn-1-ol. The intermediate fraction (1·1 g.) appeared, from the refractive index (n_D^{20} 1·4638), to contain unchanged 3-chlorotetrahydropyran.

Under similar conditions 3-chlorotetrahydro-2-methylfuran gave pent-3-yn-1-ol (b. p. 153—160°; 28%); the 1-naphthylurethane, m. p. 119°, was undepressed by authentic material (m. p. 119°). The low-boiling fraction (b. p. 78—85°; 32%) was 2 : 3-dihydro-5-methylfuran (Found : C, 71·2; H, 9·5. Calc. for C_5H_8O : C, 71·4; H, 9·6%).

3-Chloro-2-ethyltetrahydrofuran gave 5-ethyl-2 : 3-dihydrofuran (34%), b. p. 100—110° (Found : C, 73·2; H, 10·3. Calc. for $C_6H_{10}O$: C, 73·4; H, 10·3%), and hex-3-yn-1-ol (20%), b. p. 164—166°. The 1-naphthylurethane of the latter had m. p. 85° (Sondheimer, *loc. cit.*, gives m. p. 84—85°).

3-Chlorotetrahydro-2-*iso*propylfuran gave 2 : 3-dihydro-5-*iso*propylfuran (37%), b. p. 120—127° (Found : C, 74·2; H, 10·7. Calc. for $C_7H_{12}O$: C, 74·95; H, 10·8%), and 5-methylhex-3-yn-1-ol (17%), b. p. 160—163°, which formed a 1-*naphthylurethane*, m. p. 88° (Found: C, 76·7; H, 6·7. $C_{18}H_{19}O_2N$ requires C, 76·9; H, 6·8%).

When 2 : 3-dihydro-5-methylfuran, 2 : 3-dihydrofuran, and 3 : 4-dihydropyran were stirred with sodamide in liquid ammonia, no acetylenic alcohol was formed.

2-*Formyl*-3 : 4-*dihydropyran*.—Redistilled 96% acraldehyde (295 g.), benzene (350 ml.), and quinol (4 g.) were placed in a stainless-steel autoclave (1 l.) fitted with a magnetically operated stirrer. The temperature was raised rapidly to 160° and kept just above this figure for 4 hr. The product was distilled through a 30-cm. Dufton column to give, after removal of the benzene and acraldehyde, 2-formyl-3 : 4-dihydropyran (108 g., 37%), b. p. 52—53°/17 mm., n_D^{20} 1·4646. FIAT Final Report 1157, p. 13, gives b. p. 49°/14 mm., n_D^{20} 1·4660. There were 53 g. of resinous residue.

Tetrahydro-2-hydroxymethylpyran.—Formyldihydropyran (149 g.) was hydrogenated (4 hr.) at 60°/30 atm. in ethanol (88 g.) and benzene (88 g.) with Raney nickel catalyst (21 g.). Distillation gave tetrahydro-2-hydroxymethylpyran (126 g., 81%), b. p. 182—190°, n_D^{20} 1·4566. On redistillation this had b. p. 180—183°/760 mm., n_D^{20} 1·4566 (Found : C, 61·9; H, 10·4. Calc. for $C_6H_{12}O_2$: C, 62·0 ; H, 10·3%). B.P. 595,379 gives b. p. 184—186°/760 mm., $n_D^{24\cdot5}$ 1·4565.

2-*Chloromethyltetrahydropyran*.—For our preferred procedure, see Crombie, Harper, Newman, Thompson, and Smith (preceding paper).

Di(*tetrahydropyran-2-ylmethyl*) *sulphite* was obtained by adding thionyl chloride (19 ml.) to tetrahydro-2-hydroxymethylpyran (58 g.) in pyridine (44 g.) below 25°. Stirring (3 hr.), extraction with ether (7 × 30 ml.), washing with water, drying, and distillation gave the sulphite, b. p. 135—137°/0·07 mm., n_D^{20} 1·4833 (Found : C, 51·8; H, 7·9; S, 10·4. $C_{12}H_{22}O_5S$ requires C, 51·8; H, 7·9; S, 11·5%).

Hex-5-en-1-ol.—Ring fission of 2-chloromethyltetrahydropyran (16·8 g.) with sodium (6 g.) in the usual way gave hex-5-en-1-ol (10·8 g., 86%), b. p. 152—155°, n_D^{20} 1·4348 (Found : C, 71·7; H, 12·0. $C_6H_{12}O$ requires C, 72·0; H, 12·0%). The 1-naphthylurethane had m. p. 62°.

3-*Chloro*-2-(*diethoxycarbonylmethyl*)*tetrahydropyran*.—Sodium (5·95 g.) was dissolved in anhydrous ethanol (150 ml.), and ethyl malonate (41·5 g.) added. After stirring (20 min.), 2 : 3-dichlorotetrahydropyran (31 g.) was added during 1 hr. and stirring continued (30 min.). After refluxing (30 min.), part of the solvent was removed under reduced pressure and water added. The product was thoroughly extracted with ether, the solvent evaporated, and the residue distilled. After elimination of low-boiling material a fraction, b. p. >70°/0·3 mm., n_D^{15} 1·4575 (7·4 g.), was obtained. When purified by two further distillations the *diester* (3·0 g.) had b. p. 110—115°/0·08 mm., n_D^{15} 1·4642 (Found : C, 51·9; H, 6·7; Cl, 12·9. $C_{12}H_{19}O_5Cl$ requires C, 51·7; H, 6·85; Cl, 12·7%).

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