228. *The Reaction of Chlorine with Tetrahydro-2-methylenefuran.*

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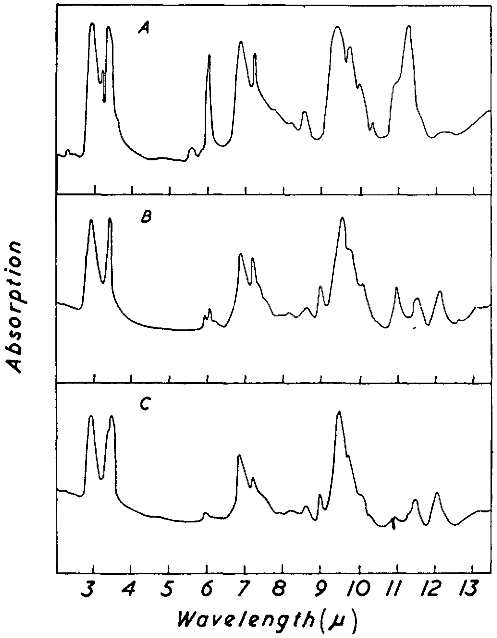
Reaction of chlorine with tetrahydro-2-methylenefuran is shown to give 2 : 3-dichlorotetrahydro-2-methylfuran, 2-chlorotetrahydrofurfuryl chloride, 2-chlorotetrahydro-2-methylfuran, and tetrahydrofurfuryl chloride. The preparation of 4-methylpent-4-en-1-ol from 3-halogenotetrahydro-3-methylpyran is described.

The ring scission of cyclic β-halogeno-ethers by sodium to yield alkenols is well established and is applicable whether the β-halogen atom is attached to the ring [1,2,3] or to a side-chain.[4,5] The latter class of compounds is not readily available, and a possible route to one type, the addition of chlorine to tetrahydro-2-methylenefuran (VIII) followed by replacement of the α-halogen atom by an alkyl group by means of a Grignard reagent, has been investigated.



A, 4-*Methylpent*-4-*en*-1-*ol.* *B, Mixture of* 4-*methylpent*-3-*en*-1-*ol and* 4-*methylpent*-4-*en*-1-*ol.* *C,* 4-*Methylpent*-3-*en*-1-*ol.* Absorption at 11·27 and 6·03 μ is characteristic of $>C=CH_2$ group.

Tetrahydro-2-methylenefuran (VIII) has been prepared [6,7] (in 30% yield of redistilled material) by dehydrohalogenation of tetrahydrofurfuryl bromide with powdered potassium hydroxide. We have found it preferable to use the more readily available tetrahydrofurfuryl chloride [3] and diethylene glycol as a solvent, a 68% yield being then obtained. It is of interest that Paul and Tchelitcheff prepared 2 : 3-dihydro-5-methylfuran (IV) from tetrahydrofurfuryl bromide under these conditions. Tetrahydro-2-methylenefuran (VIII) is a labile compound isomerising to 2 : 3-dihydro-5-methylfuran when heated [7,8] (slow distillation), in the presence of acid,[9] and, as we have found, on storage. As a consequence

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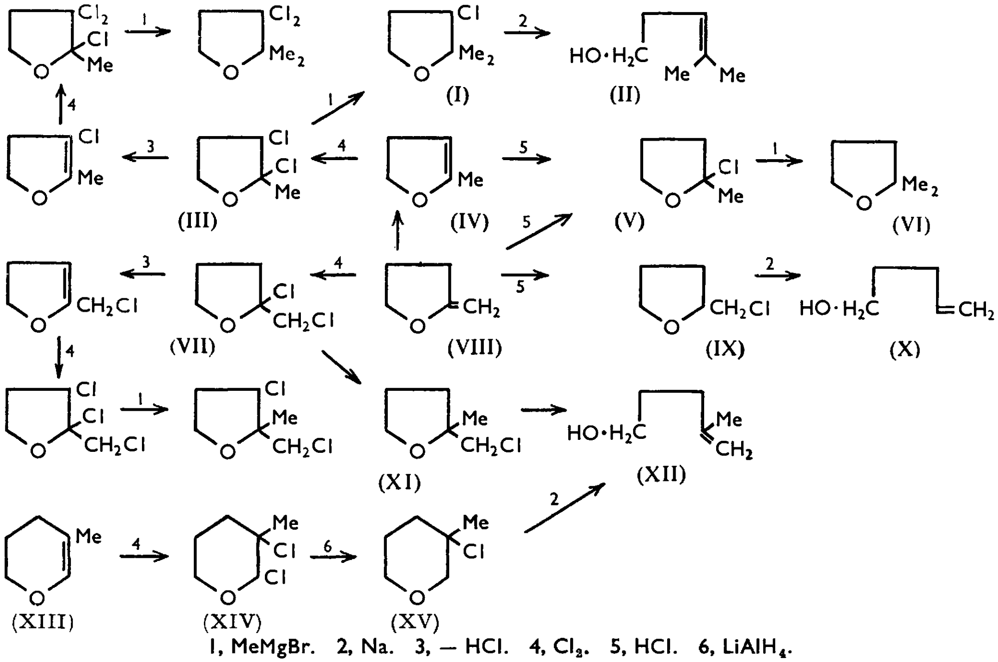
[1] Crombie and Harper, *J.*, 1950, 1707, 1714.
[2] Ansell and Selleck, *J.*, 1956, 1238.
[3] Ansell and Brown, *J.*, 1957, 1788.
[4] Brooks and Snyder, *Org. Synth.*, Coll. Vol. III, 1955, p. 698.
[5] Ficini, *Bull. Soc. chim. France*, 1956, **23**, 119.
[6] Paul, *ibid.*, 1933, **53**, 417.
[7] Paul and Tchelitcheff, *ibid.*, 1950, **17**, 520.
[8] Eglinton, Jones, and Whiting, *J.*, 1952, 2873.
[9] Thomas and Wilson, *J. Amer. Chem. Soc.*, 1951, **73**, 4803.

its preparation must be carried out expeditiously and it must be used immediately. The acid-catalysed conversion of the isomer with the exocyclic double bond to that with the endocyclic double bond is paralleled by that of methylene*cyclo*pentane to methyl*cyclo*pentene[10] and is at variance with the generalisation of Brown, Brewster, and Shechter[11] (which they consider applicable to the tetrahydrofuran ring) that " reactions will proceed in such a manner to favour the formation or retention of an exo double bond in a 5-ring."

In an attempt to avoid, or at least minimise, isomerisation of the methylene compound during its reaction with chlorine, it was added to chlorine at −60° and the reaction mixture immediately added to an excess of methylmagnesium bromide. Distillation gave tetrahydro-2 : 2-dimethylfuran (VI) (2·5%), a middle fraction, from which material giving analyses for chlorotetrahydrodimethylfuran could be isolated, and a higher-boiling dichlorotetrahydrodimethylfuran fraction (13%). Ring scission with sodium of the above middle fraction gave pent-4-en-1-ol (X) (14%), and a mixture (44·5%) of 4-methylpent-3-en-1-ol (II) with some 4-methylpent-4-en-1-ol (XII) [the presence of the latter was identified from the infrared spectrum of the ring-scission product of a purified sample of the chlorotetrahydrodimethylfuran fraction, although absorption at 11 μ may indicate the presence of yet another component (see diagram)]. These compounds are derived from tetrahydrofurfuryl chloride (IX), 3-chlorotetrahydro-2 : 2-dimethylfuran (I), and 2-methyltetrahydrofurfuryl chloride (XI), and together with the isolation of tetrahydro-2 : 2-dimethylfuran (VI) imply the formation in the chlorination step of 2-chlorotetrahydro-2-methylfuran (V), tetrahydrofurfuryl chloride (IX), 2 : 3-dichlorotetrahydro-2-methylfuran (III), and 2-chlorotetrahydrofurfuryl chloride (VII). The formation of the first pair (V and IX) necessitates the addition of hydrogen chloride to tetrahydro-2-methylenefuran (VIII) and possibly 2 : 3-dihydro-5-methylfuran (IV); and formation of the latter pair (III and VII) necessitates the addition of chlorine to the same unsaturated compounds. This is illustrated in the annexed scheme, in which the initial product 2-chlorotetrahydrofurfuryl chloride (VII) is considered to eliminate hydrogen chloride which is known to catalyse the



1, MeMgBr. 2, Na. 3, − HCl. 4, Cl_2. 5, HCl. 6, $LiAlH_4$.

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[10] Turner and Garner, *J. Amer. Chem. Soc.*, 1957, **79**, 253.

[11] Brown, Brewster, and Shechter, *ibid.*, 1954, **76**, 467.

conversion of the methylene compound (VIII) into 2 : 3-dihydro-5-methylfuran (IV). The reaction scheme also illustrates the formation of more highly chlorinated products.

In a separate experiment the addition of hydrogen chloride to tetrahydro-2-methylenefuran (VIII), followed by treatment with methylmagnesium bromide, was shown to yield tetrahydro-2 : 2-dimethylfuran (VI) and tetrahydrofurfuryl chloride. The comparable experiment with 2 : 3-dihydro-5-methylfuran (IV) has been reported [7] also to yield tetrahydro-2 : 2-dimethylfuran. We have confirmed this and obtained no indication of the formation of 3-chlorotetrahydro-2-methylfuran.

In order to identify 4-methylpent-4-en-1-ol (XII) among the above reaction products an authentic sample was prepared by the ring scission with sodium of both 3-bromo- and 3-chloro-tetrahydro-3-methylpyran (XV). These were obtained respectively by treatment of 2 : 3-dibromo- and 2 : 3-dichloro-tetrahydro-3-methylpyran (XIV) [from 3 : 4-dihydro-5-methyl-2*H*-pyran [12] (XIII)] with lithium aluminium hydride, which has been shown [3, 13] to reduce αβ-dihalogeno-ethers to β-halogeno-ethers.

From the above results it is apparent that, owing to the complexity of the reaction, the chlorination of tetrahydro-2-methylenefuran, followed by treatment with a Grignard reagent and ring scission of the β-halogeno-ethers produced, is not a satisfactory route to structurally homogeneous alkenols.

EXPERIMENTAL

In distillations marked (S) a 100 × 0·6 cm. spinning-band fractionating column (E. Haage, Mülheim) was used.

Tetrahydro-2-methylenefuran.—Tetrahydrofurfuryl chloride [3] (480 g.) was added to a cold solution of potassium hydroxide (448 g.) in diethylene glycol (1 l.). A fast stream of dry nitrogen was passed through the mixture which was gradually warmed to 105—115°; distillation commenced and a fairly vigorous exothermic reaction ensued. After this had subsided the internal temperature was raised to 155°. The distillate, collected over potassium carbonate, separated into two layers. The upper organic layer was removed, dried (powdered KOH), and rapidly distilled to yield tetrahydro-2-methylenefuran (253 g., 75%), b. p. 98—104°, n_D^{20} 1·4490. Distillation (from powdered KOH) through a 25 × 2 cm. Vigreux column gave material (228 g., 68%) of b. p. 101—102°, n_D^{20} 1·4485. Eglinton, Jones, and Whiting [8] record b. p. 100—102°, n_D^{19} 1·4490; Paul and Tchelitcheff [7] record b. p. 98—99°, n_D^{19} 1·4476.

Reaction of Methylmagnesium Bromide with the Chlorination Products of Tetrahydro-2-methylenefuran.—Tetrahydro-2-methylenefuran (168 g., 2 moles), dissolved in dry methylene chloride (180 ml.), was added to a solution of chlorine (136 g., 1·9 moles) in the same solvent (250 ml.) maintained at −50°. The resulting cold solution was added to a stirred solution of methylmagnesium bromide [from magnesium 63·2 g. (2·6 g.-atoms) in ether (600 ml.)]. Refluxing of the solvent resulted and a white solid separated. On completion of the addition the mixture was stirred for a further 1 hr. and then poured on crushed ice and ammonium chloride. The organic layer was separated and the aqueous layer extracted with ether. Distillation of the dried ($MgSO_4$) combined extracts through a 40 × 2 cm. helix-packed column gave the following fractions: (*a*) tetrahydro-2 : 2-dimethylfuran (5 g.), b. p. 86—93°, n_D^{20} 1·4100—1·4108 (b. p. 88—92° on redistillation from sodium) (Found: C, 72·25; H, 11·6. Calc. for $C_6H_{12}O$: C, 72·0; H, 12·0%) (Colonge and Garnier [14] record b. p. 93°, $n_D^{18\cdot5}$ 1·4088; Paul and Tchelitcheff [7] record b. p. 91—92°, $n_D^{19\cdot5}$ 1·4262; Yur'ev Kondrat'eva, and Akishin [15] record b. p. 92·2—92·4°, n_D^{20} 1·4045), (*b*) (130 g.), b. p. 142—151°, n_D^{20} 1·4463—1·4510, and (*c*) (44 g.), b. p. 25—55°/0·3 mm., n_D^{20} 1·4630—1·4750, which on redistillation gave a mixture of dichlorotetrahydrodimethylfurans, b. p. 64—65°/4 mm., n_D^{20} 1·4839 (Found: C, 42·5; H, 5·9; Cl, 42·0. Calc. for $C_6H_{10}OCl_2$: C, 41·9; H, 6·0; Cl, 42·6%). Distillation (S) of a portion (12 g.) of fraction (*b*) gave a mixture (4·6 g.) of compounds (XI and I), b. p. 139—143°, n_D^{20} 1·4458 (Found: Cl, 25·9. Calc. for $C_6H_{11}OCl$: 26·4%), and indications of material, b. p. >149°, n_D^{20} >1·4500 (cf. tetrahydrofurfuryl

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[12] Ansell and Gadsby, unpublished work.

[13] Crombie, Gold, Harper, and Stokes, *J.*, 1956, 136.

[14] Colonge and Garnier, *Bull. Soc. chim. France*, 1948, **15**, 432.

[15] Yur'ev, Kondrat'eva, and Akishin, *Zhur. obschei Khim.*, 1953, **23**, 1944.

chloride, b. p. 151—152°, n_D^{20} 1·4550). Ring scission with sodium (as described below) of the remainder (118 g.) gave substantially pure pent-4-en-1-ol (22 g.), b. p. 140—148°, n_D^{20} 1·4327—1·4350. A redistilled (S) sample had b. p. 138—139°, n_D^{20} 1·4290 (Found: C, 69·8; H, 11·6. Calc. for $C_5H_{10}O$: C, 69·65; H, 11·55%); α-naphthylurethane, m. p. and mixed m. p. 62·5—63° (Crombie, Gold, Harper, and Stokes [13] record b. p. 134—137°, n_D^{20} 1·4301, and α-naphthylurethane, m. p. 62°). Hydrogenation in the presence of Adams catalyst gave pentan-1-ol, b. p. 136—138°, n_D^{20} 1·4104 (α-naphthylurethane, m. p. 65—66°) (Huston and Agett [16] record b. p. 135—137°, n_D^{20} 1·4110, and α-naphthylurethane, m. p. 65·5°) together with a mixture (81 g.), b. p. 153—156°, n_D^{20} 1·4427—1·4444, of 4-methylpent-3-en-1-ol and 4-methylpent-4-en-1-ol (identified from infrared spectrum; for preparation see below) which gave the *α-naphthylurethane* of the former, m. p. and mixed m. p. 85—86° (Found: N, 5·3. $C_{17}H_{19}O_2N$ requires N, 5·2%). Ansell and Brown [3] record b. p. 157—158°, n_D^{19} 1·4452, for 4-methylpent-3-en-1-ol. For constants of 4-methylpent-4-en-1-ol see below. The infrared spectrum of the mixture of isomeric alcohols obtained from ring scission of the redistilled fraction (free from tetrahydrofurfuryl chloride) was determined (see diagram).

Essentially the same results were obtained when chlorine was replaced by bromine, but the intermediates were less stable.

Addition of Hydrogen Chloride to Tetrahydro-2-methylenefuran and 2 : 3-Dihydro-5-methylfuran.—Dry hydrogen chloride (32 g., 0·88 mole) was passed into a solution of tetrahydro-2-methylenefuran (74 g.) in ether (200 ml.) at −60° to −65° and the resulting cold solution added to a stirred solution of methylmagnesium bromide (from magnesium, 31 g.) in ether (300 ml.) so that gentle refluxing was maintained. After being stirred for a further 1 hr. the mixture was worked up as after addition of chlorine. Distillation gave tetrahydro-2 : 2-dimethylfuran (46 g., 52%), b. p. 92°, n_D^{20} 1·4094, and, after a small (*ca.* 1 g.) intermediate cut, tetrahydrofurfuryl chloride (13 g., 12%), b. p. 147—153°, n_D^{20} 1·4548—1·4552. Ring scission of the last chloride gave pent-4-en-1-ol, b. p. 136—137° (α-naphthylurethane, m. p. 62°) (cf. above).

In a similar experiment with 2 : 3-dihydro-5-methylfuran, tetrahydro-2 : 2-dimethylfuran, b. p. 92°, n_D^{20} 1·4102, was obtained together with material of high b. p. No evidence of an appreciable quantity of 3-chlorotetrahydro-2-methylfuran was obtained (cf. Paul and Tchelitcheff [7]).

3-Halogenotetrahydro-3-methylpyran.—A solution of 2 : 3-dihalogenotetrahydro-3-methylpyran [12] [from 3 : 4-dihydro-5-methyl-2*H*-pyran (60 g., 0·6 mole)] in ether (120 ml.) was added to a stirred suspension of lithium aluminium hydride (8·5 g. of 85% purity, equiv. to 0·18 mole) in ether (300 ml.) so that vigorous refluxing was maintained. The mixture was boiled and stirred for a further 1 hr. and then decomposed (caution; cf. ref. 17) by the addition of wet ether and then water. The ethereal solution was decanted from the residual solid which was washed with ether by decantation. The combined extracts were washed with 10% sodium hydroxide solution, then with water, and dried ($MgSO_4$). Distillation gave in one case *3-bromotetrahydro-3-methylpyran* (71 g., 61%), b. p. 67—72°/20 mm., n_D^{20} 1·4902—1·4904 (an analytical sample had b. p. 71°/20 mm., n_D^{20} 1·4903) (Found: C, 40·6; H, 6·4; Br, 44·3. $C_6H_{11}OBr$ requires C, 40·3; H, 6·2; Br, 44·7%), and in the other *3-chlorotetrahydro-3-methylpyran* (55·5 g., 70%), b. p. 66—69°/37 mm., n_D^{20} 1·4553 (an analytical sample had b. p. 68°/36 mm., n_D^{20} 1·4577) (Found: C, 53·9; H, 8·3; Cl, 25·9. $C_6H_{11}OCl$ requires C, 53·6; H, 8·2; Cl, 26·4%).

4-Methylpent-4-en-1-ol.—A little 3-halogenotetrahydro-3-methylpyran was added to a suspension of powdered sodium (19 g.) in ether (50 ml.), and the mixture stirred until reaction commenced as indicated by boiling of the ether and appearance of a blue colour on the surface of the sodium. Ether (100 ml.) was added, followed by the remainder of the 3-halogenotetrahydro-3-methylpyran (0·4 mole in all) in ether (100 ml.), so as to maintain vigorous boiling. After being stirred for a further 2 hr., the mixture was decomposed by the cautious addition of water. The ether layer was separated and the aqueous layer extracted with ether (2 × 100 ml.). Distillation of the dried ($MgSO_4$) combined extracts gave *4-methylpent-4-en-1-ol* (65% from 3-bromo and 85% from 3-chloro), b. p. 64—68°/20 mm., n_D^{20} 1·4382. A redistilled (S) sample had b. p. 67·5—68°/19 mm., n_D^{20} 1·4372 (Found: C, 71·7; H, 12·2. $C_6H_{12}O$ requires C, 71·95; H, 12·1%). The derived *α-naphthylurethane* [needles from light petroleum (b. p. 40—60°)] had m. p. 52—53° (Found: C, 75·5; H, 7·4; N, 5·15. $C_{17}H_{19}O_2N$ requires C, 75·8; H, 7·1; N, 5·2%).

[16] Huston and Agett, *J. Org. Chem.*, 1941, **6**, 123.
[17] Bessant, *Chem. and Ind.*, 1957, 432.

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