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RESEARCHES ON OXYGEN RING COMPOUNDS

IV. Alkenylation of Furfuryl Acetate with Diene Hydrochlorides

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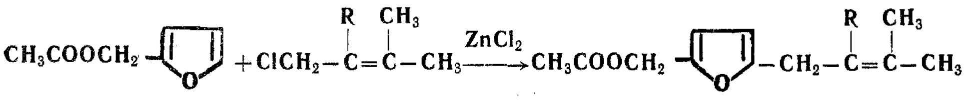
Treatment of furfuryl acetate with equilibrium mixtures of 1, 2 and 1, 4 hydrochlorides of isoprene and dimethylbutadiene respectively give 2-(3-methylbuten-2-yl)-5-acetoxymethylfuran and 2-(2, 3-dimethylbuten-2-yl)-5-acetoxymethylfuran, further hydrolyzed to the corresponding 5-alkenylfurfuryl alcohols.

At present indirect methods are used to prepare [1-3] comparatively little investigated homologs of furfuryl alcohol with a substituent at position 5. The present authors have previously reported alkenylation of furan [4] and sylvan [5] by diene hydrochlorides, in the presence of zinc chloride and zinc acetate to accept the hydrogen chloride. The present paper extends this method to furfuryl acetate, whose alkylation with isoprene and dimethylbutadiene hydrochlorides (equilibrium mixtures of 1, 2 and 1, 4 isomers) gives 5-alkenylfurfuryl acetates



I $R=H$; II $R=CH_3$

The structures of the reaction products are assumed by analogy with those of the alkenylation of sylvan with diene hydrochlorides [5]. The order of addition of reagents given in the experimental section is that generally recommended for alkenylating acidophobic furan compounds with diene hydrochlorides.

Hydrolysis of acetates I and II gives the corresponding alcohols, characterized as their xanthates.

Experimental

2-(3-Methylbuten-2-yl)-5-acetoxymethylfuran (I). 0.2 mole furfuryl acetate in 20 ml dry ether was stirred, and 1 ml of a saturated solution of $ZnCl_2$ in ether added, followed by 0.5 ml of the total quantity of 0.2 mole isoprene hydrochloride [6]. When reaction had started (darkening of the solution), 0.3 g of the 0.16 mole anhydrous zinc acetate was added, with stirring, and stirring continued until solution was almost complete. This addition of small portions of zinc acetate and alkenyl hydrochloride was repeated 2-3 times, to ensure that reaction had begun and was proceeding normally. (If reaction had not begun, the presence of considerable amounts of alkenyl chlorides could cause uncontrolled reaction accompanied by resinification and overflowing of the reaction mixture. Excess chloride later also had to be avoided.) Then 5 g zinc acetate and 20 ml ether were introduced, and using external ice cooling, chloride was added at a rate such that the temperature did not exceed 10°. When a considerable part of the precipitate had dissolved, the remaining zinc acetate was added, then 40 ml ether, and addition of chloride was continued. Stirring was continued for 2 min after addition (which took 45-60 min) was complete, 50 ml water was added, and the mixture stirred intensively until it turned light. The ether solution was separated off, washed with water, then with $NaHCO_3$ solution, and dried over $MgSO_4$. The ether was distilled off, and the residue distilled under reduced pressure to give unchanged furfuryl acetate (0.11 mole) bp 85-87° (30 mm) and reaction product I. Yield of I 41%, based on the reacted furfuryl acetate; it had bp 110° (3 mm); d_4^{20} 1.0321; n_D^{20} 1.4858. Found: C 69.22; H 8.18%, ester no. 267.9; MR_D 57.8. Calculated for $C_{12}H_{16}O_3$: C 69.40; H 7.76%, ester no. 269.0; MR_D 57.6.

2-(2,3-Dimethylbuten-2-yl)-5-acetoxymethylfuran (II). Prepared from furfuryl acetate and dimethylbutadiene hydrochloride [7] in a way similar to the above. Alkenylchloride addition took 25-30 min. Yield 27%, bp 126-127° (3.5 mm); d_4^{20} 1.0292; n_D^{20} 1.4870. Found: C 70.09; H 8.18%, ester no. 256.7, MR_D 62.0. Calculated for $C_{13}H_{18}O_3$: C 70.03; H 8.20%, ester no. 251.9, MR_D 62.2.

2-(3-Methylbuten-2-yl)-5-hydroxymethylfuran. 2.9 g I was refluxed for 1 hr with 15 ml 10% alcoholic KOH, 150 ml water added, the whole extracted with ether, the extract dried over $MgSO_4$, then distilled under reduced pressure, to give a 73% yield bp 115 (3.5 mm), d_4^{20} 1.0178; N_D^{20} 1.490. Found: C 72.93; H 8.87%; MR_D 47.5. Calculated for $C_{10}H_{14}O_2$: C 72.85; H 8.48%; MR_D 48.3.

Potassium xanthate mp 139-140° (from acetone + ether). Equivalent 274.5 (iodometric). Calculated for $C_{11}H_{13}KO_2S_2$: 280.5.

2-(2, 3-Dimethylbuten-2-yl)-5-hydroxymethylfuran was prepared from compound II by the preceding method. Yield 69%, bp 115° (2.5 mm); d_4^{20} 1.0111; n_D^{20} 1.4945. Found: C 73.32; H 9.11%; MR_D 51.9. Calculated for $C_{11}H_{16}O_2$: C 73.30; H 8.95%; MR_D 52.9.

Potassium xanthate mp 148-149° (from acetone + ether). Equivalent 296.0 (iodometric). Calculated for $C_{12}H_{15}KO_2S_2$: 294.5.

REFERENCES

1. J. Colonge and A. Girantet, Bull., 1166, 1962.
2. R. Tiwari and N. Srivastava, Rec. trav. chim., 75, 254, 1956.
3. A. L. Midzhoyan and V. G. Afrikyan, DAN ArmSSR, 25, 201, 1957.
4. Yu. I. Tarnopol'skii and V. N. Belov, ZhOrKh, 1, 595, 1965.
5. Yu. I. Tarnopol'skii and V. N. Belov, KhGS [Chemistry of Heterocyclic Compounds], 648, 1965.
6. A. Ultee, J. Chem. Soc., 530, 1943.
7. L. Hatch and G. Jourey, J. Am. Chem. Soc., 75, 3712, 1953.

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