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RESEARCHES ON OXYGEN RING COMPOUNDS

III. Alkenylation of Sylvan with Diene Hydrochlorides*

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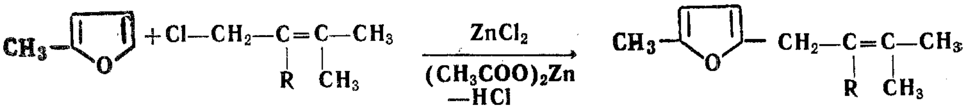
Treatment of sylvan with equilibrium mixtures of 1, 2- and 1, 4-hydrochlorides of isoprene and dimethylbutadiene in the presence of zinc chloride and acetate gives the 2-methyl-5-alkenylfurans corresponding to the 1, 4-hydrochlorides of the dienes, which are further hydrolyzed to unsaturated γ-diketones.

Previously [1] the present authors reported alkenylation of furan with hydrochlorides of dienes in the presence of $ZnCl_2$ and $(AcO)_2Zn$. It is of interest to extend this method to furan homologs and derivatives where there is increased electronic density in the ring, which it has hitherto not been possible to alkylate with halogen compounds under the usual Friedel-Crafts conditions. The present paper describes alkenylation of sylvan (I) with isoprene and dimethylbutadiene hydrochlorides.

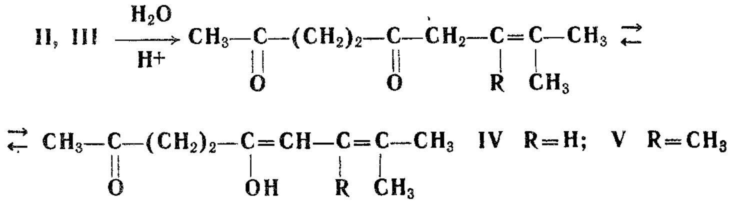


I

II R=H; III R=CH_3

The diene hydrochlorides were used as their 1, 2 and 1, 4 isomer equilibrium mixtures [2, 3]. Ozonolysis shows that the only products are II and III, corresponding to the 1, 4 isomers of the hydrochlorides.

Under acid hydrolysis conditions [4] the furans II and III give respectively the unsaturated γ-diketones IV and V, the position of the double bond being proved by ozonolysis.



$$\text{II, III} \xrightarrow[H^+]{H_2O} CH_3-\underset{O}{\underset{\|}{C}}-(CH_2)_2-\underset{O}{\underset{\|}{C}}-CH_2-\underset{R}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-CH_3 \rightleftarrows$$

$$\rightleftarrows CH_3-\underset{O}{\underset{\|}{C}}-(CH_2)_2-\underset{OH}{\underset{|}{C}}=CH-\underset{R}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-CH_3 \quad \text{IV } R=H; \ \text{V } R=CH_3$$

The diketones IV and V cannot be cyclized to cyclopentenones by the Hundsiecker method [4], and this may be because the carbonyl group homoallylic to the double bond enolizes. The observed molecular refractions of the diketones lie between those calculated for diketones and conjugated ketodienols.

Allyl bromide does not react with sylvan under the conditions used. The violent reaction between hydrochlorides of dienes and 2-vinylfuran leads to complete resinification.

Experimental

Sylvan was prepared by hydrogenating furfural at atmospheric pressure in the presence of finely divided copper [5]. The diene hydrochlorides were prepared from the corresponding dienes [2, 3]. A SF-4 instrument was used to determine the UV spectra over the range 216-300 mμ in isooctane.**

2-Methyl-5-(3-methylbuten-2-yl) furan (II). To 8.2 g (0.1 mole) sylvan in 20 ml dry ether was added 1 ml catalyst (a saturated solution of anhydrous zinc chloride in dry ether), 0.5 g anhydrous $(AcO)_2Zn$, and about 1 ml of a total amount of 5.2 g (0.05 mole) mixed isoprene hydrochlorides, the mixture stirred till reaction began (color changed, $(AcO)_2Zn$ dissolved), when it was cooled to 0°-5°, and the following added: 9.5 g $(AcO)_2Zn$, 20 ml ether, and the rest of the hydrochloride dropwise over 20-30 min (30 ml ether being added after 10 min), after which the stirring was con-

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*For Part II see [1].

**The spectra were determined by G. D. Kayukova (VNIISNDV).

tinued for 5 min more. The product was washed with water, then with saturated $NaHCO_3$ solution, and dried over $MgSO_4$. The ether was distilled off, and the residue distilled under reduced pressure, yield 3.5 g (47%) II, bp 99° (30 mm); d_4^{20} 0.9090; n_D^{20} 1.4762. Found: C 80.14; H 9.41 %; MR_D 46.5. Calculated for $C_{10}H_{14}O$; C 80.00; H 9.35%; MR_D 46.7. UV spectrum: λ_{max}, mμ (log ε): 223 (4.02), 273 (2.43), 276 (2.43). It did not give a maleic anhydride adduct.

2-Methyl-5-(2,3-dimethylbuten-2-yl) furan (III). This was prepared by the above method from sylvan and mixed dimethylbutadiene hydrochlorides, yield 40%. Bp 104° (30 mm); d_4^{20} 0.9245; n_D^{20} 1.4785. Found: C 80.48; H 9.81%: MR_D 50.3. Calculated for $C_{11}H_{16}O$: C 80.44; H 9.82%; MR_D 51.3. UV spectrum: λ_{max} mμ (log ε): 222 (4.00), 271 (2.54), 277 (2.57).

Maleic anhydride adduct of III. For its preparation see [1]. Mp 78° (from ether). Found: C 68.70; H 7.07%: Calculated for $C_{15}H_{18}O_4$: C 68.69; H 6.92%. Reaction of equimolecular amounts of sylvan and diene hydrochlorides gave 25-30% yield of II and III.

2-Methylnonen-2-dione-5, 8 (IV). 0.15 mole II was refluxed and stirred with 10 ml AcOH, 10 ml water, and 1 ml 5% H_2SO_4 for 10 hr, 50 ml water added, the ether extract washed with saturated $NaHCO_3$ solution, then with water, dried over $MgSO_4$, the ether distilled off, and the residue distilled under reduced pressure. Yield 39%. Tollens reaction negative. Bp 104-106° (3 mm), d_4^{20} 0.9606; n_D^{20} 1.4865. Found: C 71.24; H 9.74%; MR_D 50.2. Calculated for $C_{10}H_{16}O_2$: C 71.15; H 9.55%; MR_D 47.9 (diketone); 50.8 (ketonedienol).

Bis-2,4-dinitrophenylhydrazone, mp 145-146° (from alcohol). Found: N 21.17%. Calculated for $C_{22}H_{24}N_8O_8$: N 21.20%.

2, 3-Dimethylnonen-2-dione-5, 8 (V) was prepared by the above method, yield 37%. Negative Tollens reaction. Bp 114-116° (3 mm); d_4^{20} 0.9761; n_D^{20} 1.4896. Found: C 72.79; H 10.07%; MR_D 53.5. Calculated for $C_{11}H_{18}O_2$: C 72.49; H 9.95%; MR_D 52.6 (diketone); 55.5 (ketodienol).

Bis-2, 4-dinitrophenylhydrazone mp 142-143° (from alcohol). Found: N 20.53%, Calculated for $C_{23}H_{26}N_8O_8$: N 20.65%.

Ozonolysis. The furans II and III were ozonized as previously described [1]; chromatographing the products led to the isolation of only acetone, as its 2, 4-dinitrophenylhydrazone, mp 125°. Diketones IV and V were ozonized in ethyl acetate. The ozonides of diketone IV were refluxed with aqueous $NaHCO_3$ solution, and after acidifying, distillation gave ethyl acetate and acetone, the 2, 4-dinitrophenylhydrazone of the latter having mp 125°. Isobutyric aldehyde was not found.

Decomposition of the ozonides of diketone V with 30% hydrogen peroxide followed by steam distillation gave a distillate in which only acetone was detected. Mixed mp of the 2, 4-dinitrophenylhydrazone with an authentic specimen was undepressed.

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