RESEARCHES ON COMPOUNDS WITH OXYGEN IN THE HETEROCYCLIC RING

Alkylating Furan Compounds with Tertiary Chlorides and Cinnamyl Chloride*

Yu. I. Tarnopol'skii, I. S. Shraiber, and V. N. Belov

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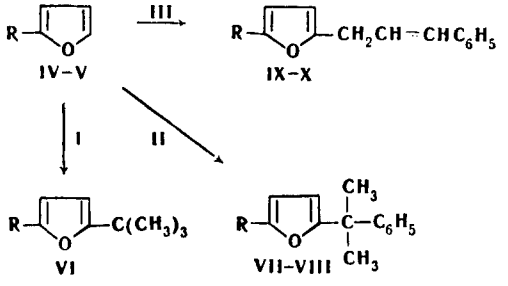
Alkylation of furan and sylvan with 2-phenyl-2-chloropropane and cinnamyl chloride, and alkylation of sylvan with tert-butyl chloride in the presence of zinc chloride and zinc acetate are described.

We previously described [1–3] alkylation of acidophobic furan compounds with hydrochlorides of dienes in the presence of zinc chloride and zinc acetate as acceptors for hydrogen chloride. The present work extends that method to some other reactive chlorides: tert-butyl chloride (I); 2-phenyl-2-chloropropane (II), and cinnamyl chloride (III).



IV, VII, IX R = H; V, VI, VIII, X R = CH_3

It was not possible to alkylate the furan IV with chloride I. Compounds VIII, IX, and X were synthesized by the methods described for alkylation of sylvan with diene hydrochlorides [2]. Ozonolysis established the position of the double bond in compounds IX and X. Compounds VI and VII were accompanied by large quantities of side reaction products formed by the action of zinc acetate on the chlorides. The low-boiling cuts obtained in the alkylation of sylvan V with chloride I evidently consisted of tert-butyl acetate and diisobutene.

EXPERIMENTAL

2-(2-Phenylpropyl-2)furan (VII). 0.5 g $ZnCl_2$ was added to a mixture of 0.15 mole chloride II and 0.45 mole furan IV, the whole stirred until reaction began (darkening of the solution), and then 0.1 mole zinc acetate added in small portions, the first five portions being added only after most of the preceding one had dissolved. Later when a considerable excess of zinc acetate was present, the temperature was 15°. When addition of the zinc acetate was complete (1 hr), 50 ml water was added, the mixture stirred vigorously, the organic layer washed with water and then with $NaHCO_3$ solution, dried over $MgSO_4$, and the furan distilled off. The residue was vacuum-distilled, to give VII (see table).

Further distillation gave α-methylstyrene dimerization products, yield 9.3 g, bp 150°–160° (2 mm), n_D^{20} 1.5662; bromine number 61.2, calculated 67.5. The literature gives [5] bp 158°–160° (2 mm), n_D^{20} 1.5680–1.5660; bromine number 62.7.

Compound VI was prepared similarly (see table). In the same way a fraction bp 95–105° was obtained, containing saponified and unsaturated compounds.

Ozonolysis of compounds IX and X. 0.5 ml compound was ozonized in 10 ml ethyl acetate. The solution of ozonizes was shaken with 3 ml saturated $NaHSO_3$ solution, acidified with H_2SO_4, and steam-distilled. In the distillate benzaldehyde was detected as its 2,4-dinitrophenylhydrazone mp 235–236° (ex EtOH), undepressed mixed mp with an authentic specimen.

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*For Part IV see [1].

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Mendeleev Moscow Institute of Chemical Technology

Furan and Sylvan Alkylation Products

Compound	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Formula	Found, % C	Found, % H	Calculated, % C	Calculated, % H	Yield, %
2-Methyl-5-tert-butylfuran (VI)	140 (760)	0.8732	1.4465	42.3	42.3	$C_9H_{14}O$	78.28	10.13	78.02	10.21	12.5
2-(2-Phenylpropyl-2)furan (VII)	124—125 (21)	1.0081	1.5250	56.6	57.6	$C_{13}H_{14}O$	83.53	7.68	83.83	7.58	40
2-Methyl-5-(2-phenylpropyl-2)furan (VIII)	119—120 (10)	1.0183	1.5311	61.1	62.3	$C_{14}H_{16}O$	83.85	8.04	83.98	8.05	60
2-(3-Phenylpropen-2-yl)furan* (IX)	138—140 (10)	1.0444	1.5738	58.2	57.2	$C_{13}H_{12}O$	84.86	6.65	84.75	6.57	31
2-Methyl-2-(3-phenylpropen-2-yl) furan (X)	125 (1.5)	1.0301	1.5671	60.0	61.5	$C_{14}H_{14}O$	84.81	7.18	84.91	7.12	37

*The literature [4] gives bp 146.5°–147° (13 mm); d_4^{20} 1.029; n_D^{20} 1.552.