STUDY OF FURAN COMPOUNDS

XLVI * REACTION OF MONOBROMO DERIVATIVES OF

1,6-DIOXASPIRO[4,4]NONANES WITH SODIUM METAL

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4,5-Dihydrofuranyl-3-alkanole (II) are formed by the reaction of monobromo derivatives of 1,6-dioxaspiro[4.4]nonanes (I) with sodium metal in dry ether. II are readily converted to 1,6-dioxaspiro[4.4]nonanes (III) as a result of intramolecular cyclization.

This paper is devoted to a clarification of the question of whether the bromo derivatives of spirans III will react with metals, particularly sodium, as a consequence of their acetal nature. In analogy with the literature data [2-4] on the reactions of metals (mainly sodium and magnesium) with halocetals, one might have expected the formation of unusual, unsaturated alcohol ethers, vis., γ -hydroxy derivatives of 4,5-di-hydrofuran. It turned out that the expected reaction product – 4,5-dihydrofuranyl alcohol – can be isolated only in the case of the simplest bromospiran – 4-bromo-1,6-dioxaspiro[4.4]nonane (Ia). The structure of the 1-(4[•],5[•]-dihydro-2[•]-furanyl)-3-propanol (IIa) obtained was confirmed by the analytical data and IR spectroscopy. The broad absorption band at 3500 cm⁻¹ corresponds to the valence vibrations of the associated OH groups. The intense band at 1030 cm⁻¹ attests to the presence of a primary alcohol group. The band at 1660 cm⁻¹ is characteristic for the valence vibrations of the C=C bond in the 4,5 dihydrofuran ring [5].

Dihydrofuranyl alcohols II were not isolated by the action of sodium on monobromo-substituted alkylspirans Ib-e; the reaction products (60-70%) were the corresponding spirans (III, Table 1). However, it may be assumed that the formation of the latter proceeds through a step involving dihydrofuranyl alcohols II, traces of which are detected in the reaction products by IR spectroscopy.



*See [1] for Communication XLV.

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| IABLE 1. Results | or the rea | CCLION OL INION | 0110.100 | 111Sanc- | urea r'a | -DIOXa | spiro[4.4]NO | nanes | WILD | sodiu | E Me | etal |
|--|----------------------|-----------------------|------------------------------|------------|----------|--------|---|----------------|----------------|--------------|--|-------|
| | | , , | n _D ²⁰ | | IW | R_D | Emnirica1 | а 1 | 70 5 | 01°. | oto | Viald |
| Reaction Product | Starting compound | b, در (press., mm) | > | d_4^{20} | Found | Calc. | formula | C C | , и, <i>и</i> | Calc Calc | A H | 4° |
| 0 - cH2 - cH2 - 0H | Ia | 106-107 (14) | 1,4778 | 1,036 | 34,34 | 35,03 | $C_7H_{12}O_2$ | 65,31 65,41 | 9,53 9,49 | 65,59 | 9,44 | 70 |
| CH ₃ | 4 | 49—50 (8) | 1,4387 | 0,9659 | 42,37 | 42,65 | C ₉ H ₁₆ O ₂ | 68,52 68,42 | 10,28 10,70 | 69,29 | 10,33 | 9 |
| CH ₃ -C ₂ H ₅ | Ŋ | 93—94 (25) | 1,4442 | 0,9604 | 47,09 | 47,27 | $C_{10}H_{18}O_{2}$ | 70,13 70,08 | 10,35 10,14 | 70,55 | 10,66 | 65 |
| $c_{H_3} \xrightarrow{C_{H_3}} c_{2^{H_5}} \ddagger$ | PI | 88—89 (23) | 1,4408 | 0,9426 | 51,61 | 51,88 | C11H20O2 | 71,78 | 10,84 | 69'12 | 10,94 | 70 |
| $cH_3 - cH_3$ iso $c_3 u_2$ | le | 84—86 (10) | 1,4470 | | _ | Identi | fied by IR spect | roscopy | | | ···· · · · · · · · · · · · · · · · · · | 64 |
| | - | | | | | | | | | | | |

-Substituted 1.6-Dioxasniro[4.4]Nonanes With Sodium Metal Results of the Reaction of Monohromo-TABLE 1.

*According to [6], bp 167-169 deg (760 mm), nD²⁰ 1.4385. † According to [7], bp 92-94 deg (25 mm), nD²⁰ 1.4445. ‡ According to [7], bp 91-93 deg (25 mm), nD²⁰ 1.4408. **According to [8], bp 109-111 deg (25 mm), nD²⁰ 1.4465.

Carbonium ion IV, in which the acetal bonds can be cleaved in the 1 or 2 directions to form sodium derivatives V or VI, respectively, is probably formed initially. It is well known that compounds containing an exocyclic double bond are less stable than their isomers with an endocyclic bond, i.e., the formation of structure V is energetically more favorable. In addition, when there are a different number of alkyl substituents in the 2 and 7 positions of the spiran ring one should take into account the relative stability of primary, secondary and tertiary radicals in the acetals, which determine the case of cleavage of the unequivalent rings in spirans III [9]. A direct proof of the intramolecular cyclization of alcohols II to spirans III was the spontaneous conversion of dihydrofuranyl alcohol IIa to 1,6-dioxaspiro[4.4]nonane (IIIa) during storage, as confirmed by IR spectroscopy (disappearance of the ν_{OH} 3500 cm⁻¹, $\nu_{C} = C$ 1660 cm⁻¹, and $\nu = CH$ 3090 cm⁻¹ absorption bands and the appearance of all frequencies characteristic for the spectrum of IIIa).

$$\bigcup_{\substack{I \in H_2 - CH_2 - CH_2 \\ II a}} \stackrel{OH}{\longrightarrow} \bigcup_{\substack{I \in H_2 \\ III a}} \stackrel{OH}{\longrightarrow} \bigcup_{\substack{III A}} \stackrel{OH}{\longrightarrow} \bigcup_{\substack{II A}} \stackrel{OH}{\longrightarrow} \bigcap_{\substack{II A} \stackrel{OH}{\longrightarrow} \bigcap_{\substack{II A}} \stackrel{OH}{\longrightarrow} \bigcap_{\substack{II A} \stackrel{OH}{\bigoplus} \bigcap_{\substack{II A} \stackrel{OH}{\bigoplus$$

The equilibrium in the isomerization of dihydrofuranyl alcohols II is consequently shifted to favor the formation of the spirocyclic system, which is promoted by the accumulation of alkyl substituents in the ring and side chain of II.

In contrast to dihydrofuranyl alcohols II, the ketones of this series are stable compounds [10] because of the absence of the electrophilic hydrogen of the hydroxyl group which is capable of adding to the double bond.

Our results with respect to the intramolecular cyclization of 4,5-dihydrofuranyl alcohols to spirans III are yet another proof of the mechanism for the formation of these spirans during catalytic hydrogenation of furan compounds, as theoretically and experimentally correlated in [6,11].

EXPERIMENTAL

Bromospiran Ia, and monobromo-substituted 2,7-dimethyl-(Ib), 2-methyl-8-ethyl- (Ic), 2,7-dimethyl-7-ethyl-(Id), and 2,7-dimethyl-9-isopropyl-1,6-dioxaspiro[4.4]nonane (Ie) were prepared by the method described in [12, 13].

The general method for the reaction of bromospirans I with sodium metal is as follows. Sodium metal (0.04-0.1 mole) was added gradually (in 30-40 min) to 0.02-0.05 mole of I dissolved in a threefold amount of absolute ether. The reaction mixture was then heated with vigorous stirring under moderate reflux for 5-7 h. A white crystalline precipitate of sodium bromide was formed even during the addition of the first portions of sodium, and the amount of this precipitate increased as the reaction continued. At the end of the reaction, the residual sodium was thoroughly removed with a filter gauze, and water (50-70 ml) was added to the filtrate (which contains sodium bromide) to dissolve the precipitate and decompose the alkoxide. The ether layer was separated, and product was extracted from the aqueous layer with ether. The combined ether extracts were washed with water and dried with calcined magnesium sulfate. After removal of the ether, the residue was vacuum distilled.

The results of the reaction of sodium with bromospirans I are presented in Table 1. The identity of III with the previously known spirans was confirmed by their identical physical constants, IR spectra, and analytical data.

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