

**OPENING OF THE FURAN RING:  
REACTION OF 6 $\beta$ -HYDROXYFUROEREMOPHILANE  
WITH ACTIVATED SILICA GEL\***

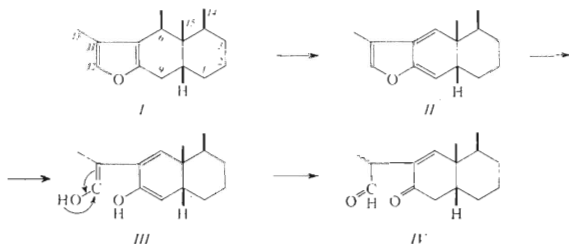
L. NOVOTNÝ and K. KOTVA

*Institute of Organic Chemistry and Biochemistry,  
Czechoslovak Academy of Sciences, 166 10 Prague 6*

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The opening of the furan ring of 6 $\beta$ -hydroxyfuroeremophilane by contact reaction with active silica gel is described, giving rise to  $\alpha,\beta$ -unsaturated ketoaldehyde *IV*.

Active adsorbents, primarily alumina and silica gel, when in contact with some organic substances cause deep structural changes which may sometimes be utilized for preparative purposes<sup>1</sup>. The main prerequisite for reactions of this type are both a suitable arrangement of functional groups and  $\pi$ -electron systems, and further the possibility for the active surface to exert an effect on the adsorbed substrate. In practice this means that the substance is either soluble in a non-polar solvent, for example pentane, which does not affect the adsorbent activity, or — in the case of more polar substances — it is necessary to choose the reverse procedure, *i.e.* the substance dissolved in polar solvent is mixed with excess adsorbent, the solvent is eliminated by evaporation in a vacuum, and the adsorbent is activated by heating.



\* Part CCXXXI in the series on Terpenes; Part CCXXX: This Journal 39, 480 (1974).

During the isolations and separations of substances of furoeremophilane type<sup>2</sup> we observed that when chromatographed on more active adsorbents they sometimes underwent irreversible changes. In this communication we described the reaction of petasalbin (*I*; 6 $\beta$ -hydroxyfuroeremophilane)<sup>3</sup> with silica gel.\* On the active surface of silica gel a splitting off of the C<sub>(6)</sub>-hydroxyl group first takes place under formation of the dehydration product *II*. In a subsequent reaction this gives with water an unstable hydration product, *III*, which stabilizes immediately to compound *IV*.

$\alpha,\beta$ -Unsaturated ketoaldehyde *IV* of the composition C<sub>15</sub>H<sub>22</sub>O<sub>2</sub> displays in its IR spectrum bands of an aldehyde group at 1712 and 2720 cm<sup>-1</sup> and an  $\alpha,\beta$ -unsaturated ketone (in the six-membered ring) at 1672 cm<sup>-1</sup>. Its PMR spectrum is also in agreement with the supposed structure.

### EXPERIMENTAL

A solution of petasalbin *I* (0.5 g) in pentane (15 ml) was added to 10 g of silica gel (0.03–0.06 mm) freshly activated by 6 hours' heating at 120°C *in vacuo*. Silica gel immediately assumed a red colour. The mixture was refluxed for 30 minutes in a bath at 50°C. After cooling water (10 ml) was added gradually to the mixture which changed its colour to green. After elution with methanol, evaporation, dissolution of the residue in ether and drying of the ethereal solution over sodium sulfate the mixture was chromatographed on silica gel. Elution with a mixture of light petroleum and ether (4:1) gave an oil which was distilled at 180°C (bath temperature) and 0.5 Torr. Yield 355 mg. For C<sub>15</sub>H<sub>22</sub>O<sub>2</sub> (234.3) calculated: 76.88% C, 9.46% H; found: 76.90% C, 9.55% H.

PMR spectrum:  $\text{CH}=\text{O}$ : 9.59 p.p.m.;  $\text{O}=\text{C}-\text{C}=\text{CH}$ : 6.58 p.p.m.;  $\text{CH}_3-\text{CH} \begin{matrix} \text{CHO} \\ \text{C}=\end{matrix}$ : 1.19 d,  $J = 7.1$  Hz; sec methyl (H<sub>14</sub>): 0.91 p.p.m. d,  $J = 6.6$  Hz; angular methyl H<sub>15</sub>: 1.11 p.p.m. s;  $\text{CH}_3-\text{CH} \begin{matrix} \text{CHO} \\ \text{C}=\end{matrix}$ : 3.55 p.p.m. (determined by double resonance).

### REFERENCES

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2. Šorm F.: *Pure Appl. Chem.* 21, 263 (1970).
3. Novotný L., Herout V., Šorm F.: *This Journal* 27, 1400 (1962).

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\* In formula *I* OH group in position 6 is missing.