

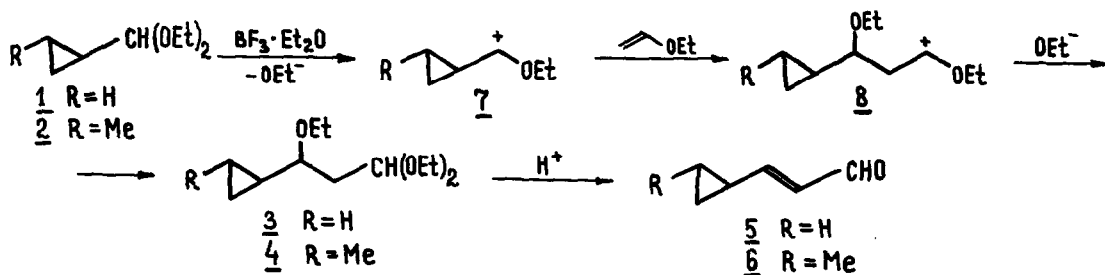
CONDENSATION OF CYCLOPROPANECARBOXALDEHYDE ACETALS WITH VINYLETHYL ETHER
 SYNTHESIS OF ACETALS OF FORMYLVINYL CYCLOPROPANE AND FORMYLBICYCLOPROPANE

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(Received in UK 7 December 1976; accepted for publication 2 February 1977)

We have examined the reaction between cyclopropanecarboxaldehyde acetals and vinyl ethers in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$. It was found that diethyl acetals of 1-formyl-2-methylcyclopropane 1 and 1-formylcyclopropane 2 reacted with equimolar quantity of vinylethyl ether in the presence of catalytic quantity of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in normal conditions¹⁾ to form only adducts in ratio 1:1 as well as α, β -unsaturated and aromatic aldehyde acetals¹⁾:

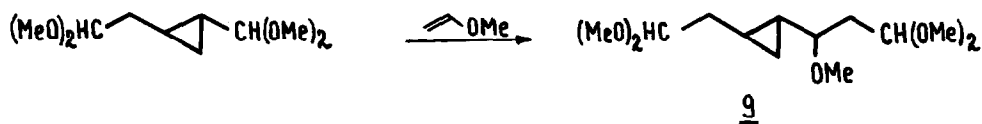


The absence in the reaction mixture of adducts of 1 and 2 with vinylethyl ether in ratio 1:2 and more was confirmed by GLC and evidenced that the carbocation 7 forming on the first stage of reaction was stabilized by cyclopropane ring to a greater extent than by CH_2 group in carbocation 8.

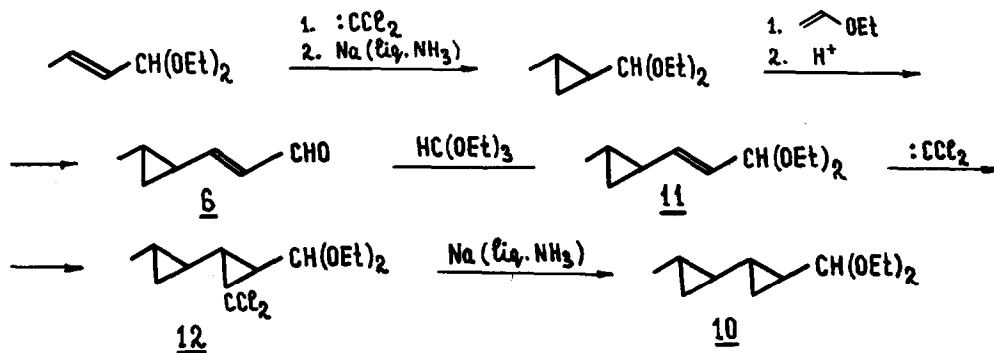


Etoxyacetals 3 and 4 are easily hydrolyzed by the mixture of AcOH-AcONa-H₂O¹⁾ to form previously unknown β -formylvinylcyclopropanes 5 and 6.

The addition of vinylmethyl ether to bis (dimethyl) acetal of 1-formyl-2-(formylmethyl) cyclopropane proceeded only at the acetal group closest to the cycle as well as in the case of glutaric aldehyde acetal where the reaction with vinyl ether was brought about at the acetal group adjacent to the double bond¹⁾:

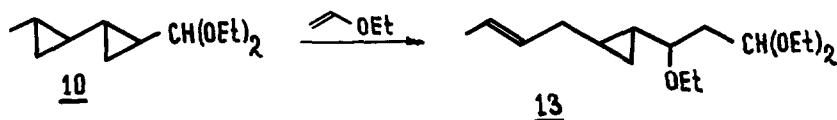


On the basis of our results we carried out the first synthesis of bicyclopentanecarboxaldehyde diethyl acetal 10 by the following scheme:

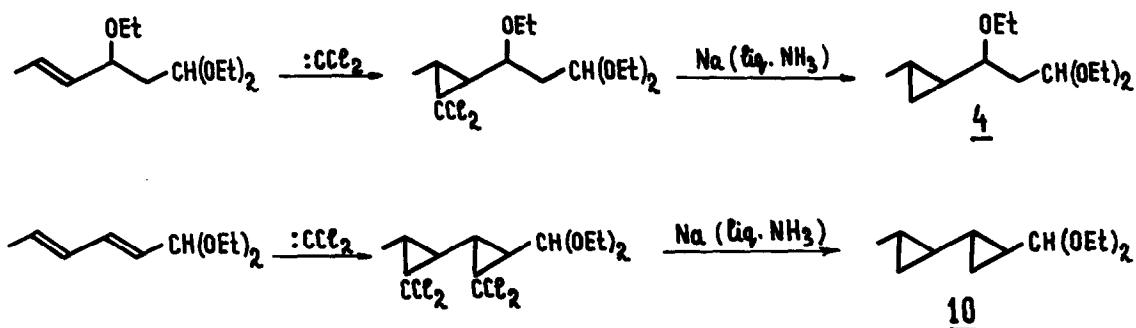


Acetal 2 was obtained in accordance with our previous works^{2,3)}.

We tried to obtain also tricyclopentanecarboxaldehyde acetal from acetal 10 by the above scheme. However, the reaction between 10 and vinyl ethyl ether in normal conditions and even at -40° was accompanied by the opening of the ring which was remote from the acetal group:



The structure of 4 and 10 was confirmed by an unambiguous synthesis:



The elemental analyses of compounds 3, 4, 9, 10, 11, 12, 13 and 14 were in good accordance with theoretical data. The structures of compounds 3, 4, 5, 6, 9, 10, 11, 12, 13, 14 were also confirmed by the PMR-spectra. Yields and some physical properties of compounds obtained are given in table 1.

Table 1

Compound	Yield %	B.p. °C/mm	n_D^{20}
<u>3</u>	45	108-109/16	1.4250
<u>4</u>	70	98-102/6	1.4350
<u>5</u> [≡]	81	73-75/15	1.5015
<u>6</u> ^{≡≡}	86	76-77/16	1.5012
<u>9</u>	70	114-116/0.6	1.4390
<u>10</u>	75	92-95/11	1.4352
<u>11</u>	60	94-95/15	1.4465
<u>12</u>	65	93/0.5	1.4605
<u>13</u>	65	120/0.2	1.4443
<u>14</u>	78	120-125/0.5	1.4840

$\equiv \nu_{CO}(CCl_4) 1695 \text{ cm}^{-1}; \lambda_{MAX}^{EtOH} 246 \text{ nm } (\epsilon 16200); 2,4\text{-dinitrophenylhydrazone, m.p. } 174-175^\circ.$

$\equiv \equiv \nu_{CO}(CCl_4) 1690 \text{ cm}^{-1}; \lambda_{MAX}^{EtOH} 251 \text{ nm } (\epsilon 16900); 2,4\text{-dinitrophenylhydrazone, m.p. } 161-162^\circ.$

Thus, we found for the first time a reaction in which cyclopropane ring shows the π -system properties without the opening of the cycle. The reaction of cyclopropanecarboxaldehyde acetals with vinyl ethers is an efficient path to elongate the side carbon chain of cyclopropane ring. Cyclopropanecarboxaldehyde acetals are convenient initial compounds for the bicyclopropanecarboxaldehyde acetals synthesis.

References

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3. A.Kh.Khusid, G.V.Kryshtal, V.F.Kucherov, L.A.Yanovskaya, Izvestiya Akademii USSR, seriya khim., 1975, 2787.