NOTES

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On the Mechanism of Formation of Furotropones from (4-Halogeno-2-butenyloxy)tropones

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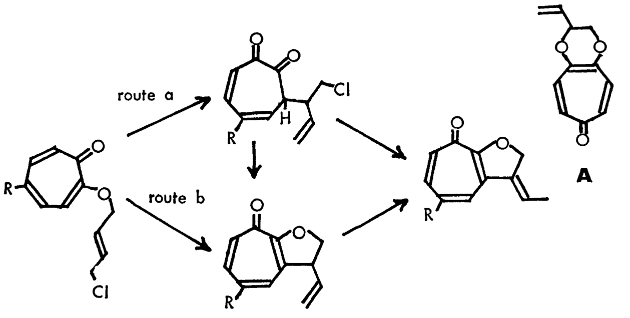
Synopsis. Pyrolysis of 2-[(*E*)-4-bromo-3-butenyloxy]tropone and 2-[(*E*)-4-bromo-2-methyl-2-butenyloxy]tropone produced 3-methyl-3-vinyl-2,3-dihydro-8*H*-cyclohepta[*b*]furan-8-one and 3-isopropylidene-2,3-dihydro-8*H*-cyclohepta[*b*]furan-8-one, which established the involvement of 3,3-sigmatropy for furotropone formation.

Previously, the one-step production of furotropones and difurotropones by application of the Claisen rearrangement to some bifunctional troponyl allyl ethers has been reported.[1,2] There are two possible mechanisms, *i.e.*, route a, 3,3-sigmatropy followed by dehydrohalogenation, and route b, a direct S_N2'-type elimination from the allyl ethers.[3]



R=H, OH or O-CH_2CH=H-CH_2Cl

Chart 1.

It is important to establish the mechanism to discover the synthetic versatility for furotropones. Using an unsymmetrical halogenide, (*E*)-1,4-dibromo-2-methyl-2-butene (**1**), route a was shown to be correct by the following experiments.[4]

1 was introduced into an anhydrous solution of potassium tropolonate, prepared from tropolone (**2**), potassium hydroxide and 18-crown-6-(CE) in benzene, and refluxed for 7 h to form the isomeric ethers, **3** and **4**. The ethers were separated by high-pressure liquid chromatography. The major product (**3**), a colorless liquid, 35%, was shown to be 2-[(*E*)-4-bromo-3-methyl-2-butenyloxy]tropone [δ[5]:1.89(3H, d, J=1 Hz), 3.97(2H, s), 4.68(2H, d, J=6 Hz), 5.89(1H, tq, J=6, 1Hz), and 6.6—7.3(5H, m)] and **4**, a colorless liquid, 18% identified as 2-[(*E*)-4-bromo-2-methyl-2-butenyloxy]tropone [δ:1.83(3H, d, J=1 Hz), 4.01(2H, s), 4.57(2H, s), 5.91(1H, tq, J=8, 1 Hz), and 6.6—7.2 (5H, m)].

The *o*-dichlorobenzene solution of **3** when heated at 180 °C for 10 min gave product **5**, a colorless liquid, 13% yield other than the deallylation product, **2**. The NMR spectrum of **5**[δ:1.47(3H, s), 4.42(1H, d, J=13 Hz), 4.49(1H, d, J=13 Hz), 5.19(1H, d, J=17 Hz), 5.27(1H, d, J=10 Hz), 6.98(1H, dd, J=17, 10 Hz), and 6.8—7.2(4H, m)] was deduced as 3-methyl-3-vinyl-2,3-dihydro-8*H*-cyclohepta[*b*]furan-8-one. Similarly, **4** afforded **6**, a colorless liquid, 24%, together with 45% of deallylated **2**. The NMR spectrum of **6** [δ: 1.80(3H, t, J=2 Hz), 2.12(3H, t, J=3 Hz), 5.20 (2H, m), and 6.6—7.2(4H, m)] was compatible with 3-isopropylidene-2,3-dihydro-7*H*-cyclohepta[*b*]furan-8-one.

The specific formation of **5** from **3** and **6** from **4** established the involvement of 3,3-sigmatropy followed by dehydrobromination. Consequently the previous results may be interpreted in terms of a 3,3-process.

The absence of primary rearrangement products is thought to be a facile cyclization into the dihydrofuran derivatives. Kitahara *et al.*[6] observed the spontaneous cyclization of 3-allyltropolone when treated with bromine.

Experimental

*Reaction of Tropolone (2) with (*E*)-1,4-Dibromo-2-methyl-2-butene (1): Formation of Isomeric Ethers, 3 and 4.* The

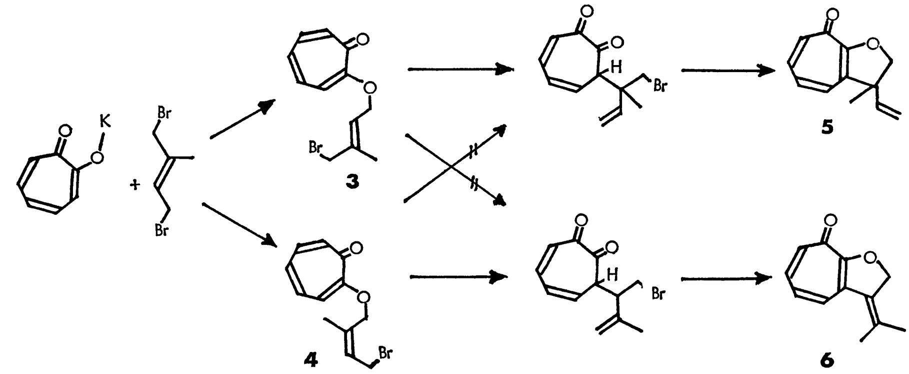


Chart 2.

potsasium salt of **2** (275 mg), the crown ether (CE, 450 mg) and **1**$^{7)}$ (1.0 ml) were mixed in benzene (20 ml) and refluxed for 7 h. The mixture was, after removal of the solvent, fractionated on a silica gel column to give colorless liquids, **4**, 46 mg (10%) [Found: *m/e*, 268, 270 (M^+, double peaks for $C_{12}H_{13}O_2Br$). ν: 2980, 1625, 1595, 1580, 1490, 1285, 1190, 1090 cm^{-1}], from benzene–ether (80 : 20), and **3**, 170 mg (37%) [Found: 268, 270 (M^+). ν: 2980, 1625, 1595, 1580, 1490, 1290, 1195, 1092 cm^{-1}], from the same solvent. Analytical samples were obtained by high-pressure liquid chromatography (Micropolasil, hexane–ethyl acetate).

*Thermal Reaction of **3**: Formation of **5**.* An *o*-dichlorobenzene solution (5 ml) of **3** (35.8 mg) was heated on an oil bath and refluxed for 10 min. Silica gel column chromatography of the mixture produced **2**, 3.5 mg (37%), and subsequently a colorless oil, **5**, 1.9 mg (13%) [Found: C, 76.30; H, 6.59%. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%. ν: 2900, 1615, 1565, 1480, 1430, 1000 cm^{-1}].

*Thermal Reaction of **4**: Formation of **6**.* Similarly, **4** (22 mg) was heated in *o*-dichlorobenzene (5 ml), and refluxed for 10 min. Silica gel chromatography of the mixture gave a colorless oil, **6**, 2.2 mg (24 %) [Found: *m/e*, 188.0722 (M^+). Calcd for $C_{12}H_{12}O_2$: 188.0769. ν: 2980, 1615, 1570, 1480, 1430 cm^{-1}], together with hydrolyzed **2**, 2.7 mg (45%).

References

1) H. Takeshita, I. Kouno, and K. Miyake, *Kyushu Daigaku Seisan Kagaku Kenkyusho Hokoku*, **66,** 1 (1977).

2) H. Takeshita, K. Tajiri, and I. Kouno, *Heterocycles*, **6**, 1101 (1977).

3) A dihydro-1,4-dioxin derivative (**A**) has been isolated in the condensation reaction of 5-hydroxytropolone and *trans*-1,4-dichloro-2-butene.

4) The condensation of **2** to *trans*-1,4-dichloro-2-pentene was unsuccessful.

5) The NMR spectra were obtained in $CDCl_3$ solutions at 100 MHz by a JEOL FX 100 Model spectrometer, and the chemical shifts expressed in δ values from the internal standard, Me_4Si.

6) H. Shimanouchi, T. Ashida, Y. Sasada, M. Kakudo, I. Murata, and Y. Kitahara, *Bull. Chem. Soc. Jpn.*, **40**, 779 (1967).

7) **1** was prepared by the bromination of isoprene in CCl_4 solution, and was used without purification. Gas-liquid chromatographic analysis revealed the presence of isomers (less than 10%).