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Unusual Rearrangement of (Cyclopropylmethoxy)benzene and Its Derivatives in the Presence of $BF_3 \cdot Et_2O$

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Abstract—(Cyclopropylmethoxy)benzene and its *ortho*- and *para*-bromo-substituted analogs in the presence of $BF_3 \cdot Et_2O$ undergo rearrangement with formation of (cyclobutyloxy)benzene and 2-ethyl-2,3-dihydro-1-benzofuran.

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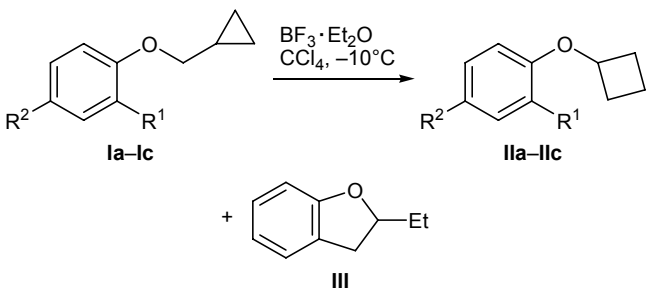
Rearrangement of allyl phenyl ethers into allylphenols (Claisen rearrangement) have become a model of many pericyclic [3,3]-sigmatropic reactions [1–4]. The resulting *o*- and/or *p*-allylphenols are widely used in organic synthesis as important intermediate products [1]. Diverse and facile transformations of cyclopropanes into various structural fragments of organic compounds have been considered in detail in numerous reviews [5–9]. However, there no published data on rearrangements of (cyclopropylmethoxy)benzene derivatives under the Claisen reaction conditions; such rearrangements could give rise to *o*-(but-2-en-1-yl)-phenols as a result of cleavage of the three-membered ring.

In the present work we examined transformations of (cyclopropylmethoxy)benzene (**Ia**) and its 2- and 4-bromo derivatives **Ib** and **Ic** in the presence of a Lewis acid, boron trifluoride–diethyl ether complex.

Scheme 1.



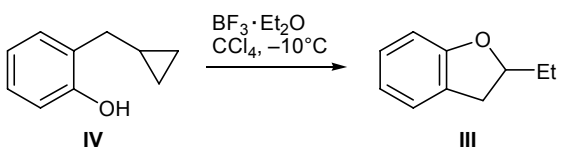
Ia–Ic **IIa–IIc** **III**

$R^1 = R^2 = H$ (**a**); $R^1 = Br$, $R^2 = H$ (**b**); $R^1 = H$, $R^2 = Br$ (**c**).

The reaction of (cyclopropylmethoxy)benzene (**Ia**) with $BF_3 \cdot Et_2O$ at a molar ratio of 2:1 in carbon tetrachloride at –10°C in 2 h afforded a mixture of (cyclobutyloxy)benzene (**IIa**) and 2-ethyl-2,3-dihydro-1-benzofuran (**III**) in 40 and 8% yield, respectively (Scheme 1). Bromo-substituted (cyclopropylmethoxy)-benzenes **Ib** and **Ic** reacted with $BF_3 \cdot Et_2O$ to produce the corresponding bromo-substituted (cyclobutyloxy)-benzenes **IIb** and **IIc** as the only products (yield 20 and 8%). In the presence of an equimolar amount of the Lewis acid, the yields of (cyclobutyloxy)benzene (**IIa**) and 2-ethyl-2,3-dihydro-1-benzofuran (**III**) decreased to 20 and 5%, respectively, whereas the yields of cyclobutyl ethers **IIb** and **IIc** increased to 45 and 53%, respectively. In no case butenyl aryl ethers were formed.

Prior to our study, isomerization of a cyclopropylmethyl fragment into cyclobutyl was reported only for cyclopropylmethanols, cyclopropanols, and their esters [5]. 2-Ethyl-2,3-dihydro-1-benzofuran (**III**) is likely to be formed as a result of unusual migration of the cyclopropylmethyl group to the *ortho* position of the aromatic ring and subsequent intramolecular ring

Scheme 2.



IV **III**

closure. This reaction path is confirmed by isomerization of *o*-(cyclopropylmethyl)phenol (**IV**) into 2-ethyl-2,3-dihydro-1-benzofuran (**III**) under analogous conditions (yield 42%; Scheme 2).

Thus (cyclopropylmethoxy)benzenes in the presence of $BF_3 \cdot Et_2O$ undergo rearrangement which involves isomerization of the cyclopropylmethyl fragment into cyclobutane ring and/or its migration into the *ortho* position of the phenyl ring and subsequent intramolecular cyclization to 2-ethyl-2,3-dihydro-1-benzofuran.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer at 300.13 and 75.47 MHz, respectively, using $CDCl_3$ as solvent and tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on a Thermo Finnigan MAT 95 XP mass spectrometer with direct sample admission into the ion source (ion source temperature 250°C; batch inlet probe temperature 50–250°C, heating rate 10 deg/min). The reaction mixtures were analyzed by GLC on a Shimadzu GL 2014 chromatograph equipped with a flame-ionization detector and a 25000 × 0.2-mm DB-35MS capillary column; carrier gas helium; the components were quantitated by the internal standard technique (decane, calibration factor 1.09).

Rearrangement of (cyclopropylmethoxy)benzenes Ia–Ic (*general procedure***).** Compound **Ia**–**Ic**, 2.0 or 4.0 mmol, was dissolved in 1.2 or 2.4 ml of carbon tetrachloride, the solution was cooled to –10°C, 0.28 g (2.0 mmol) of boron fluoride–diethyl ether complex was added under argon, and the mixture was stirred for 2 h at –10°C. The mixture was then washed with 6 ml of water at 0°C, treated with a 10% aqueous solution of sodium hydrogen carbonate until neutral reaction (pH 7), and extracted with methylene chloride (3 × 5 ml). The extracts were combined, washed with 6 ml of water, and dried over $MgSO_4$, and the solvent was removed under reduced pressure.

From 0.3 g (2.0 mmol) of (cyclopropylmethoxy)-benzene (**Ia**) we obtained 0.222 g of a dark yellow liquid. Yield of (cyclobutyloxy)benzene (**IIa**) 20%, yield of 2-ethyl-2,3-dihydro-1-benzofuran (**III**) 5%.

From 0.6 g (4.0 mmol) of (cyclopropylmethoxy)-benzene (**Ia**) we obtained 0.531 g of a dark yellow liquid. Yield of **IIa** 40%, yield of **III** 8%.

From 0.3 g (2.0 mmol) of 2-(cyclopropylmethyl)-phenol (**IV**) we obtained 0.125 g (42%) of 2-ethyl-2,3-dihydro-1-benzofuran (**III**).

(Cyclobutyloxy)benzene (IIa). Light yellow liquid. ^{1}H NMR spectrum, δ, ppm: 1.72 t (1H, CH_2, J = 8.1 Hz), 1.89 t (1H, CH_2, J = 9.5 Hz), 2.21 m (2H, CH_2), 2.48 m (2H, CH_2), 4.65 t.t (1H, CH, J = 6.8, 7.5 Hz), 6.86 d (2H, H_{arom}, J = 8.6 Hz), 6.96 t (1H, H_{arom}, J = 8.6 Hz), 7.29 d (2H, H_{arom}, J = 8.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.4 (CH_2), 30.8 (CH_2), 71.5 (CH), 115.1 (C_{arom}), 120.7 (C_{arom}), 129.5 (C_{arom}), 157.6 (C_{arom}). Mass spectrum, m/z (I_{rel}, %): 148.1 (34) $[M]^+$, 120.1 (100), 94 (54), 91.1 (34), 77 (15), 54.9 (39). Found: m/z 148.0864 $[M]^+$. $C_{10}H_{12}O$. Calculated: M 148.0888.

2-Ethyl-2,3-dihydro-1-benzofuran (III). The ^{1}H and ^{13}C NMR spectra of **III** were identical to those reported in [10].

From 0.45 g (2.0 mmol) of 2-bromo-1-(cyclopropylmethoxy)benzene (**Ib**) we obtained 0.202 g (45%) of 2-bromo-1-(cyclobutyloxy)benzene (**IIb**).

From 0.9 g (4.0 mmol) of compound **Ib** we obtained 0.183 g (20%) of cyclobutyl ether **IIb**.

2-Bromo-1-(cyclobutyloxy)benzene (IIb). Light yellow liquid. ^{1}H NMR spectrum, δ, ppm: 1.73 t (1H, CH_2, J = 8.1 Hz), 1.90 t (1H, CH_2, J = 9.5 Hz), 2.27 m (2H, CH_2), 2.49 m (2H, CH_2), 4.70 t.t (1H, CH, J = 6.8, 7.5 Hz), 6.84 t (1H, H_{arom}, J = 7.6 Hz), 6.90 d (1H, H_{arom}, J = 8.3 Hz), 7.23 d.d (1H, H_{arom}, J = 7.6, 8.3 Hz), 7.54 d (1H, H_{arom}, J = 7.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.1 (CH_2), 30.4 (CH_2), 72.3 (CH), 111.9 (CBr), 113.7 (C_{arom}), 121.5 (C_{arom}), 127.9 (C_{arom}), 133.2 (C_{arom}), 154.1 (C_{arom}). Found: m/z 225.9988 $[M - H]^+$. $C_{10}H_{11}BrO$. Calculated: M 227.10.

From 0.45 g (2.0 mmol) of 4-bromo-1-(cyclopropylmethoxy)benzene (**Ic**) we obtained 0.237 g (53%) of 4-bromo-1-(cyclobutyloxy)benzene (**IIc**).

From 0.9 g (4.0 mmol) of compound **Ic** we obtained 0.072 g (8%) of **IIc**.

4-Bromo-1-(cyclobutyloxy)benzene (IIc). Light yellow liquid. ^{1}H NMR spectrum, δ, ppm: 1.67 t (1H, CH_2, J = 8.1 Hz), 1.87 t (1H, CH_2, J = 9.5 Hz), 2.16 m (2H, CH_2), 2.44 m (2H, CH_2), 4.60 t.t (1H, CH, J = 6.8, 7.5 Hz), 6.75 d (2H, H_{arom}, J = 8.9 Hz), 7.33 d (2H, H_{arom}, J = 8.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.1 (CH_2), 30.4 (CH_2), 71.6 (CH), 112.7 (CBr), 116.7 (C_{arom}), 132.3 (C_{arom}), 158.0 (C_{arom}). Found: m/z 225.9988 $[M - H]^+$. $C_{10}H_{11}BrO$. Calculated: M 227.10.

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