

# Thermal Isomerization of 2-Bromo-2-fluoro-1-alkylidenecyclopropanes in Polar Solvents

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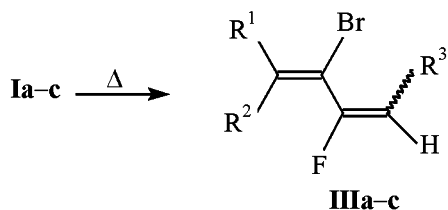
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**Abstract**—2-Bromo-2-fluoro-1-alkylidenecyclopropanes heated in polar solvents undergo isomerization into substituted 3-bromo-2-fluoro-1,3-butadienes. 2-Bromo-3-methyl-1-methylene-3-phenyl-2-fluorocyclopropane at heating afforded a mixture of substituted 1-(bromofluoromethylene)cyclopropane and isomeric 1-bromo-1-fluoro-1,3-butadienes.

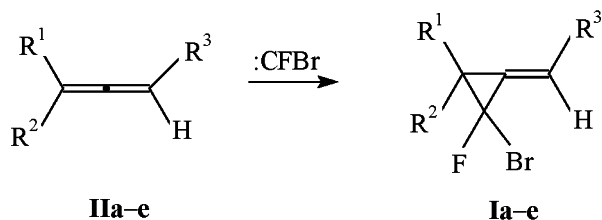
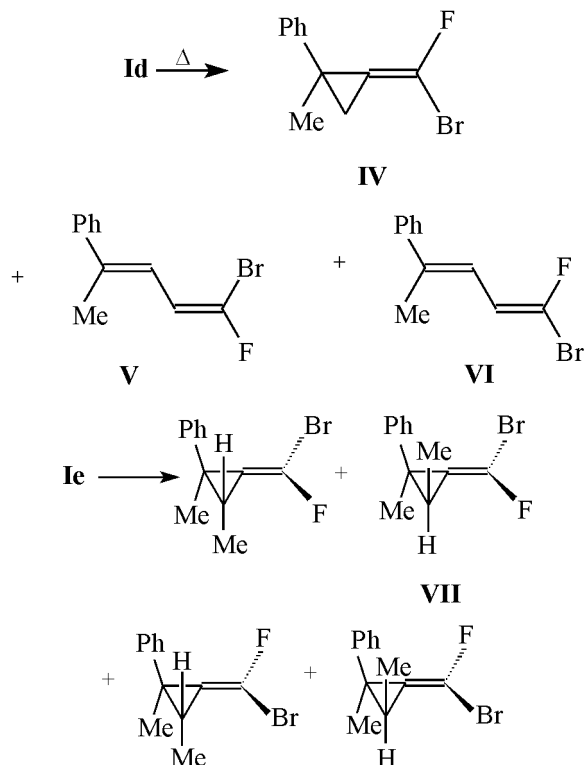
We established formerly that *gem*-dihalo-1-methylidenecyclopropanes at heating in nonpolar solvents suffered methylenecyclopropane-methylenecyclopropane rearrangement [1], whereas in polar solvents *gem*-dibromo-1-alkylidenecyclopropanes isomerized at heating into substituted 2,3-dibromo-1,3-butadienes [2].

The present report treats thermal isomerization of 2-bromo-2-fluoro-1-alkylidenecyclopropanes **Ia-e** in polar solvents. Bromofluorocyclopropanes **Ia-e** were prepared with the use of bromofluorocarbene and the appropriate allene hydrocarbons **IIa-e**. When heated in DMSO (or formamide) to 120°C bromofluorocyclopropanes **Ia-c** yielded substituted 1,3-butadienes **IIIa-c**. Compounds **IIIa-c** were isolated by preparative GLC in 42–52% yield. Their structure was established by spectral methods (see table). In the <sup>1</sup>H NMR spectra of dienes **IIIa-c** apart the proton signals from methyl groups or those from cyclobutane ring protons appear olefin proton signals ( $\delta$  5.5–6.1 ppm). After heating of bromofluoride **Id** in DMSO to 100°C for 2 h was obtained a mixture of methylenecyclopropane **IV** and isomeric 1,3-butadienes **V** and **VI** in 2:1:1 ratio. Compounds **IV–VI** were separated by preparative GLC, and their structure was established by spectral methods. In the <sup>1</sup>H NMR spectrum of compound **IV** was observed the signal from a methyl group attached to the cyclopropane ring at 1.77 ppm, doublets from cyclopropane protons at 1.92 ppm ( $J$  5 Hz) and 1.79 ppm ( $J$  5 Hz), and also proton resonances from the

aromatic ring. In the IR spectrum appeared an absorption band corresponding to an exocyclic double bond of the methylenecyclopropane moiety at 1780 cm<sup>-1</sup>.



**I–III**, R<sup>1</sup> = R<sup>2</sup> = Me, R<sup>3</sup> = H (**a**); R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = Me (**b**); R<sup>1</sup>, R<sup>2</sup> = (CH<sub>2</sub>)<sub>3</sub>, R<sup>3</sup> = H (**c**); R<sup>1</sup> = Ph, R<sup>2</sup> = Me, R<sup>3</sup> = H (**d**), R<sup>1</sup> = Ph, R<sup>2</sup> = R<sup>3</sup> = Me (**e**).



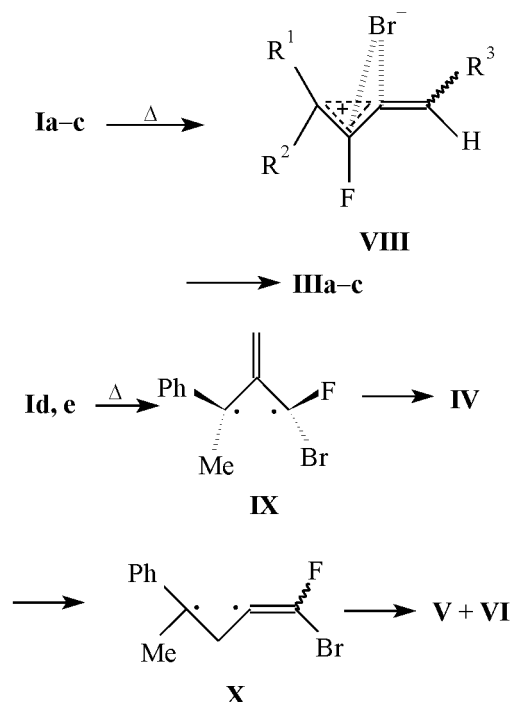
Spectral characteristics of bromofluorides **Ia-e**, **IIIa-c**, **IV-VII**

Compd. no.	IR spectrum, cm <sup>-1</sup>	<sup>1</sup> H NMR spectrum, $\delta$ , ppm ( <i>J</i> , Hz)
<b>Ia</b>	920, 945 s, 985, 1020, 1080, 1170 s, 1430, 1460, 1750, 2870, 2930, 2965, 2995	1.30 d (3H, 2), 1.34 d (3H, 2), 5.55 s (1H), 5.90 s (1H)
<b>Ib</b>	920, 1030 s, 1100, 1180 s, 1290, 1370, 1445, 1755, 2870, 2930, 2955, 2990	1.26 d (3H, 3), 1.28 d (3H, 2), 1.82 d (3H, 7), 6.26 q (1H, 7)
<b>Ic</b>	920, 955 s, 1060, 1100, 1175, 1260, 1370, 1430, 1750, 2940, 2990	1.90–2.50 (6H), 5.57 s (1H), 5.88 s (1H),
<b>Id</b>	700 s, 920, 965 s, 1030, 1070, 1115, 1175 s, 1299, 1290, 1380, 1430, 1455, 1495, 1600, 1755, 1780, 2870, 2930, 3030, 3065	1.64 d (3H, 2), 5.82 d (1H, 2), 6.06 d (1H, 2), 7.30 s (5H)
<b>Ie</b>		1.57 t (3H, 2), 1.62 t (3H, 2), 1.94 d.d (3H, 7, 4), 1.96 d.d (3H, 7, 4), 6.56 q.d (1H, 7, 2), 6.58 q.d (1H, 7, 2), 7.10–7.30 (5H)
<b>IIIa</b>	910, 1060, 1135 s, 1195 s, 1265, 1390, 1445, 1620, 2860, 2920, 2940, 2990	1.78 m (6H), 5.85 m (2H)
<b>IIIb</b>	940, 960, 1130 s, 1160, 1195, 1290, 1340, 1440 s, 1640, 1710, 2860, 2920 s, 2940, 2990	1.60–1.80 (9H), 6.13 q (1H, 7)
<b>IIIc</b>	890 s, 1070 s, 1230, 1415, 1590, 2930 s, 2960 s, 2990 s	1.90–3.20 (6H), 5.55 s (1H), 5.95 s (1H)
<b>IV</b>	700 s, 970, 1040 s, 1115 s, 1230, 1380, 1445, 1495, 1605, 1780 s, 2930, 2965, 3065	1.77 s (3H), 1.79 d (1H, 5), 1.92 d (1H, 5), 7.40–7.60 (5H)
<b>V<sup>a</sup></b>	700 s, 850, 885, 960, 1030, 1055, 112, 1170, 1250, 130, 1380, 1450, 1495, 1600 s, 1640, 3060	2.08 t (3H, 1), 6.25 d.q (1H, 11, 1), 6.49 d.d (1H, 12, 11), 7.20–7.40 (5H)
<b>VI</b>		2.06 t (3H, 1), 6.02 d.d (1H, 29, 11), 6.53 d.q (1H, 11, 1), 7.20–7.40 (5H)
<b>VII</b>	700 s, 840, 910, 930, 1030, 1100 s, 1155, 1290 s, 1375, 1450, 1495, 1600, 1755, 2930, 2985 s	0.76 d.d (3H, 6, 2), 0.77 d (3H, 7), 1.23 d.d (3H, 7, 2), 1.25 d (3H, 7), 1.45 d (3H, 2), 1.46 s (3H), 1.50 d (3H, 2), 1.51 s (3H), 1.79 q.d (1H, 6, 4), 1.81 q (1H, 6), 1.87 d.q (1H, 6, 5), 1.89 q.d (1H, 6, 5), 7.05–7.35 (Ph)

<sup>a</sup> The spectrum of compounds **V** and **VI** mixture is reported.

The reaction of bromofluorocarbene with allene **IIe** gave rise to bromofluorocyclopropane **Ie** as a mixture of two stereoisomers (see table). We failed to isolate this compound in pure state for in the course of vacuum distillation it isomerized into methylenecyclopropane **VII**. As showed the data of the <sup>1</sup>H NMR spectra, the methylenecyclopropane **VII** contained all the four possible stereoisomers.

Thus we are able to conclude that the thermal isomerization of methylenecyclopropanes **Ia-c** into dienes **IIIa-c** as also that of dibromomethylenecyclopropanes [2] proceeds via a ionic transition state **VIII**. In the process occurs simultaneous opening of the three-membered ring and bromine migration, and on the atoms of the ring arises a positive charge. Unlike that in the process of isomerization of methylenecyclopropanes **Id, e** containing aromatic substituents at the three-membered cycle occurs an opening of a carbon-carbon bond of the ring opposite to the exocyclic double bond yielding biradical **IX** and further methylenecyclopropane **IV**. Dienes **V** and **VI**



form due to the opening in the bromofluoride **IV** of the bond C<sup>1</sup>-C<sup>2</sup> in the ring via biradical (**X**).

### EXPERIMENTAL

IR spectra were recorded on spectrophotometer UR-20 from 2% solutions of compounds in CCl<sub>4</sub>. <sup>1</sup>H NMR spectra were registered for compounds **Ie**, **V-VII** from 3% solutions in CDCl<sub>3</sub> on spectrometer Bruker WM-300 (300 MHz), for the other compounds from 10% solutions in CDCl<sub>3</sub> on Tesla BS-567A instruments (100 MHz). The reaction products were separated by GLC on Tsvet=4 chromatograph, column 4000×10 mm, stationary phase E-301(25% on Chromaton N-AW-DMCS).

**2-Bromo-2-fluoro-1-alkylidenecyclopropanes Ia-e.** To a mixture of 0.1 mol of an appropriate allene **IIa-e** and 35 g of potassium tert-butyrate in 200 ml of pentane at stirring and cooling with ice as added 29 g of dibromofluoromethane in 25 ml of pentane. The reaction mixture was stirred for 4 h more, then 100 ml of water was added, organic layer was separated and dried with CaCl<sub>2</sub>. The solution was evaporated, the residue was distilled in a vacuum. Further are given the numbers of compounds, yield, %, bp, °C (mm Hg), *n*<sub>D</sub><sup>20</sup>: (**Ia**), 67, 57–60 (100), 1.4533; (**Ib**), 66, 62–64 (35), 1.4800; (**Ic**), 52, 46–47 (45), 1.4545; (**Id**), 59, 50–51 (0.1), 1.5409, bromofluoride (**Ie**) was isolated by column chromatography on silica gel, eluent pentane, yield of cyclopropane **Ie** 30%.

**2-Bromo-4-methyl-3-fluoro-1,3-pentadiene (IIIa), 4-bromo-2-methyl-3-fluoro-2,4-hexadiene (IIIb),**

**(2-bromo-1-fluoro-2-propenylidene)cyclobutane (IIIc).** A solution of 0.02 mol of an appropriate bromofluorocyclopropane **Ia-c** in 100 ml of dry DMSO was sealed in an ampule and heated to 120°C for a preset time. The ampule was cooled to room temperature, the solution was poured into 250 ml of water, extracted with ether (3×200 ml), the organic layer was separated, washed with water, and dried on MgSO<sub>4</sub>. The solvent was distilled off, and the residue was separated by preparative GLC. Further are given the numbers of compounds, duration of heating, h, yield, %, *n*<sub>D</sub><sup>20</sup>: **IIIa**, 29, 52, 1.4792; **IIIb**, 5, 42, 1.4840; **IIIc**, 52, 48, 1.5261.

**Thermolysis of 2-bromo-3-methyl-1-methylene-3-phenyl-2-fluorocyclopropane (Id).** A solution of 4.8 g (0.02 mol) of bromofluorocyclopropane **Id** in 50 ml of dry DMSO was heated for 2 h in a sealed ampule. Then the reaction mixture was worked up as described above. As showed GLC, the reaction gave rise to three products in 2:1:1 ratio. The products were separated by preparative GLC.

**1-(Bromofluoromethylene)-2,3-dimethyl-2-phenylcyclopropane (VII).** Bromofluoride **Ie** (10 g) was twice distilled in a vacuum at 3 mm Hg. Yield 7 g (70%), bp 118–120°C (3 mm Hg).

### REFERENCES

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