Journal of Fluorine Chemistry, 63 (1993) 185–191

Thermal and UV-induced isomerization of fluorinated hexatrienes

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(Received March 4, 1992; accepted August 28, 1992)

Abstract

Irradiation of octafluoro-1,3,5-hexatriene (I) in the gas phase with a high-pressure mercury lamp gave a mixture of octafluoro-2-vinylcyclobutene (III) and octafluorobicyclo[2.2.0]hex-2-ene (V). The analogous photolysis of hexatriene **I** in the liquid phase led to an equilibrium mixture of the starting compound **I** (*cis*-isomer) and the *trans*-isomer **II**, respectively. Photolysis of 2,3,4,5-tetrafluoro-1,3,5-hexatriene (VI) gave a mixture of *cis*- and *trans*-isomers, both in the vapour and liquid phases. Thermal reaction of hexatriene **I** gave octafluoro-1,3-cyclohexadiene (IV) as the sole product.

Introduction

The most interesting reactions of unsaturated compounds are associated with valence isomerization, making it possible to synthesize compounds with unusual structures and designs which are inaccessible by other synthetic methods [1]. To date, however, only a few examples of the valence isomerization of highly fluorinated olefins have been described [2–5]. The accessibility of octafluoro-1,3,5-hexatriene (I) [6] and 2,3,4,5-tetrafluoro-1,3,5-hexatriene (VI) [7] has made studies of reactions initiated either by UV light or by increased temperature on these relatively simple substrates possible.

Results

We have found that irradiation of octafluoro-1,3,5-hexatriene (I) in the vapour phase gives two valence isomers, i.e. octafluoro-2-vinylcyclobutene (III) and octafluorobicyclo[2.2.0]hex-2-ene (V) (Scheme 1). The experimental conditions employed (reaction pressure, photosensitization by mercury vapour) influenced both the mutual ratio of the isomers and the reaction rate. The

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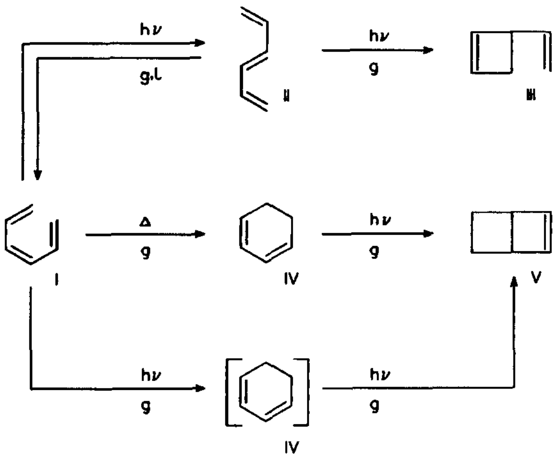


Scheme 1.

Scheme 2.

course of the reaction was accelerated by mercury vapour sensitization supporting the formation of the bicyclo derivative **V** at the expense of the cyclobutene **III**. Increase in reaction pressure resulted in a larger amount of the cyclobutene **III** and a reduction in the reaction rate. This made it possible to isolate *trans*-octafluoro-1,3,5-hexatriene (**II**) as an intermediate.

Since the cyclohexadiene **IV** was suspected as being another possible intermediate, it was prepared separately by the reaction of hexatriene **I** at elevated temperature [8] since it was not possible to trace **IV** during the photosensitized reaction. Its ready conversion to the bicyclohexene **V** under the conditions employed in this work, which were comparable to those already described [9], supports this reaction pathway.

No valence isomers of the hexatriene **I** were detected in the reaction mixture in acetone solution after irradiation with UV light. Under these conditions, only *cis–trans* isomerization occurred.

With 2,3,4,5-tetrafluoro-1,3,5-hexatriene (**VI**), reaction in either the vapour or liquid phase led to a change in the molar ratio of the *cis*- and *trans*-isomers, respectively (Scheme 2).

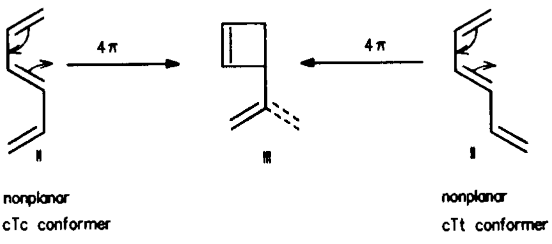
Discrimination between the *cis*- and *trans*-isomers of the hexatrienes **I** and **II** on the one hand, and the hexatrienes **VI** and **VII** on the other, was based on ^{19}F NMR spectroscopy. By using a number of the chemical shifts of the fluorine atoms located on a double bond in the highly fluorinated linear polyenes, we have found that the chemical shifts of the fluorine atoms in the *cis* configuration are shifted downfield by approximately 15–30 ppm in comparison with the chemical shifts of the *trans*-bonded atoms [7]. This has enabled a determination of the geometrical configuration on the central double bond in the symmetrical polyenes, where the vicinal interaction constant is not detectable.

The starting hexatriene **I** has been shown to exhibit a *cis* configuration relative to the internal double bond [10]. Because the *trans*-isomer **II** was found in the reaction mixture subsequent to the irradiation of **I**, we suggest that a *cis–trans* isomerization of triene **I** precedes formation of the cyclobutene **III**. The resulting process then includes a 4π electrocyclic reaction of the *trans*-hexatriene **II** to give the final product **III** (Scheme 3).

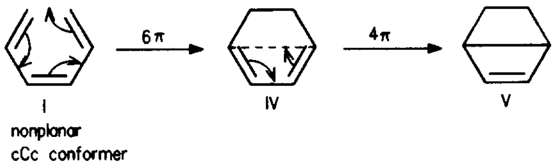
The fact that the concentration of the cyclobutene **III** increases in proportion to the decrease in the amount of the *trans*-hexatriene **II** during the reaction strongly supports this reaction mechanism.

The formation of bicyclohexene **V** is assumed to proceed via another two-step mechanism. The initial step could be accomplished via a 6π electrocyclic reaction involving the starting *cis*-isomer **I** (Scheme 4) to give cyclohexadiene **IV**. However, octafluoro-1,3-cyclohexadiene (**IV**) has been shown previously to be very unstable under these reaction conditions [9], and hence its conversion to the final bicyclohexene **V** is assumed to be very efficient and rapid. This last step should include a 4π electrocyclic reaction to yield the two four-membered rings of bicyclohexene **V**.

The different behaviours of **I** in the vapour and liquid phases are probably caused by the multiplicities of the originating excited states. The first singlet state S_1 is assumed to control the course of the vapour phase reaction. In contrast, reaction in acetone which is known to be an efficient sensitization agent may be initiated by the creation of the first triplet state T_1 of the triene **I** by energy transfer between acetone molecules in the T_1 state and triene **I** in the ground state. The results of reactions originating from the two different excited states may be quite diverse [1]. However, confirmation



Scheme 3.



Scheme 4.

of this conclusion would require a much more intimate view of the structure and energy relations between the ground and both excited states of the hexatriene **I**.

On comparing the results of the vapour-phase reactions of hexatriene **I** on one hand and of the hydrocarbon analogue on the other, it is possible to recognize substantial differences. Whilst photolysis of 1,3,5-hexatriene yields a mixture of hydrogen, benzene, 1,3-cyclohexadiene and 1,2,4-hexatriene [11, 12], the same reaction of octafluoro-1,3,5-hexatriene (**I**) leads to the exclusive formation of its valence isomers. The tendency of highly fluorinated polyenes to diminish their potential energy by the creation of either four- or six-membered rings, i.e. by increasing the number of sp^3- to sp^2-bound fluorine atoms [3], provides the driving force for the photolysis of hexatriene **I** so that valence tautomers predominate among the reaction products. However, the valence isomerization of hexatriene **VI** does not occur. It seems that the presence of the terminal $CF_2=$ group is a necessary prerequisite for electrocyclization to be initiated, allowing the above-mentioned thermodynamic effect to take place.

Experimental

Temperature values are uncorrected. Infrared spectra were measured on a Perkin-Elmer 325 instrument as solutions either in CCl_4 or $CHCl_3$. Nuclear magnetic resonance spectra were recorded on a Bruker AM 400 machine with working frequencies for ^1H and ^{19}F spectroscopy of 400.13 MHz and 376.50 MHz, respectively. All experiments were carried out in deuteriochloroform and the scale was referenced to tetramethylsilane (^1H) or trichlorofluoromethane (^{19}F) as internal standards. Mass spectra were obtained from experiments measured on a JEOL JMS-DX-303 spectrometer.

UV-induced reaction of octafluoro-1,3,5-hexatriene (I) in the vapour phase at reduced pressure

Hexatriene **I** (5.0 g, 22.4 mmol) was irradiated at 38 °C and 7.33 kPa in a 7 l photochemical reactor, using a 400 W high-pressure mercury lamp (Tesla RVK 400) situated in a quartz double-walled jacket cooled with water which was placed in the centre of the reactor. The course of the reaction was monitored by GL chromatography (dinonyl phthalate, 30 °C). The starting triene **I** disappeared after irradiation for 5 h when the crude reaction product (4.1 g) was vacuum transferred from the reaction vessel. This product contained 36% octafluoro-2-vinylcyclobutene (**III**) and 64% octafluorobicyclo[2.2.0]hex-2-ene (**V**). The titled compounds were purified by preparative GLC methods (dinonyl phthalate, 25 °C) and identified by infrared and ^{19}F NMR spectroscopy.

Octafluoro-2-vinylcyclobutene (**III**) [13]: IR (cm^{-1}): 835 (w); 870 (s); 940 (m); 1005 (m); 1080 (m); 1145 (m); 1160 (m); 1195 (w); 1215 (w); 1300 (s); 1340 (m); 1370 (w); 1390 (vs); 1780 (s) 1790 (s). ^{19}F NMR δ: 93.22 (1F, dd, $CF_2=$); 111.09 (1F, ddt, $CF_2=$); 115.03 (1F, AB, $-CF_2-$);

117.59 (1F, AB, $-CF_2-$); 124.39 (1F, s, $-CF=$); 126.62 (1F, s, $-CF=$); 162. 26 (1F, s, $-CF-$); 184.41 (1F, ddd, $-CF=CF_2$) ppm. $^2J_{FF}=190$ Hz (*gem*, $-CF_2-$); $^2J_{FF}=65$ Hz (*gem*, $CF_2=$); $^3J_{FF}=120$ Hz (*trans*, $CF_2=CF-$); $^3J_{FF}=40$ Hz (*cis*, $CF_2=CF-$).

Octafluorobicyclo[2.2.0]hex-2-ene (V) [9]: IR (cm^{-1}): 875 (m); 900 (m); 930 (m); 1020 (m); 1050 (w); 1125 (w); 1185 (s); 1195 (s); 1230 (w); 1275 (m); 1295 (w); 1330 (m); 1375 (s); 1480 (w); 1760 (m). ^{19}F NMR δ: 115.67 (2F, d, $-CF_2-$); 116.17 (2F, d, $-CF=$); 126.07 (2F, d, $-CF_2-$); 196.46 (2F, m, $-CF-$) ppm. $^2J_{FF}=215$ Hz.

Mercury-sensitized reaction of octafluoro-1,3,5-hexatriene (I)

Hexatriene **I** (2.0 g, 9 mmol) was irradiated in the same photochemical reactor described above in the presence of mercury (2.0 g). The reaction temperature and pressure were maintained at the same values as described previously. After 1 h, the amount of hexatriene **I** in the reaction mixture was negligible; at this point, 0.9 g of the crude mixture was removed and analyzed by GLC methods. An increased amount of bicyclohexene **V** (84%) was detected in the reaction product in comparison with the previous experiment.

UV-induced reaction of octafluoro-1,3,5-hexatriene (I) in the vapour phase at atmospheric pressure

Hexatriene **I** (8.0 g, 36.0 mmol) was heated to the boiling point in a 100 ml flask fitted with a 30 cm long tube made of fused silica and terminated by a water cooler. The tube containing the vapour of **I** was irradiated by means of three mercury vapour lamps (Tesla RVK 400) situated at *c.* 5 cm distance. The reaction was monitored by GLC methods. After 12 h, the largest amount of product (14%) was *trans*-octafluoro-1,3,5-hexatriène (II), which was obtained in a pure form by preparative GLC methods. The composition of the reaction mixture after 19 h was 38% cyclobutene **III**, 54% bicyclohexene **V** and 6% unchanged hexatriene **I**.

trans-Octafluoro-1,3,5-hexatriene (II) [14]: IR (cm^{-1}): 830 (m); 980 (w); 1010 (w); 1035 (w); 1125 (s); 1140 (m); 1180 (m); 1195 (s); 1265 (w); 1320 (vs); 1355 (m); 1400 (w); 1680 (w); 1750 (m); 1765 (s); 1840 (m). ^{19}F NMR δ: 91.21 (2F, dd, $CF_2=$); 104.28 (ddd, $CF_2=$); 150.67 (2F, m, $-CF=$); 184.94 (ddd, $CF_2=CF-$) ppm. $^2J_{FF}=45$ Hz (*gem*, $CF_2=$); $^3J_{FF}=115$ Hz (*trans*, $CF_2=CF-$); $^3J_{FF}=33$ Hz (*cis*, $CF_2=CF-$).

*UV-induced reaction of octafluoro-1,3-cyclohexadiene (IV) in the vapour phase**

Cyclohexadiene **IV** (2.0 g, 9.0 mmol) was completely converted to bicyclohexene **V** after 3 h interaction with UV light in the 7 l photochemical reactor using conditions similar to those described in the first experiment.

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*For comparative experiment, see ref. 9.

UV-induced reaction of octafluoro-1,3,5-hexatriene (I) in the liquid phase

A solution consisting of 3.5 g (15.6 mmol) of hexatriene **I** in 10 ml acetone was placed into the quartz tube equipped with a water cooler and irradiated with the 400 W mercury lamp whilst being stirred. After 12 h the reaction was stopped, and the reaction mixture was washed with 100 ml of water. The organic layer was dried and analyzed by GLC methods (dinonyl phthalate, 60 °C). The *cis*- and *trans*-isomers **I** and **II**, respectively, were detected as the sole fluorine-containing components of the mixture in a 44:56 ratio.

UV-induced reaction of 2,3,4,5-tetrafluoro-1,3,5-hexatriene (VI)

The same apparatus (as described above) was used for these reactions, conducted either in the vapour or liquid phase. The vapour-phase photolysis was stopped after 3 h. It was demonstrated by GLC methods (tricresyl phosphate, 60 °C) and NMR spectroscopy that the reaction product consisted of the *trans*- and *cis*-isomers of the starting compound **VI** and **VII**, respectively, in a molar ratio of 63:37.

The liquid-phase photolysis was also carried out in acetone solution. The concentration was similar to that employed in the previous experiment with triene **I**. It was found by GLC methods (tricresyl phosphate, 60 °C) that a *cis–trans* isomerization had occurred leading to the respective isomers in a mutual ratio of 42:58.

trans-2,3,4,5-Tetrafluoro-1,3,5-hexatriene (**VI**) [7]: ^{1}H NMR δ: 5.07 (2H, dm, $CH_2{=}$); 5.14 (2H, dm, $CH_2{=}$) ppm. ^{19}F NMR δ: 118.57 (2H, ddd, $CH_2{=}CF{-}$); 159.06 (2H, d, $CH_2{=}CF{-}CF{=}$) ppm. $^3J_{HF}=45$ Hz (*trans*, $CH_2{=}CF{-}$); $^3J_{FF}=26$ Hz.

cis-2,3,4,5-Tetrafluoro-1,3,5-hexatriene (**VII**) [7]: ^{1}H NMR δ: 5.07 (2H, dm, $CH_2{=}$); 5.14 (2H, dm, $CH_2{=}$) ppm. ^{19}F NMR δ: 111.79 (2F, m, $CH_2{=}CF{-}$); 138.86 (2F, m, $CH_2{=}CF{-}CF{=}$) ppm. $^3J_{FF}=18$ Hz.

Thermally-induced reaction of octafluoro-1,3,5-hexatriene (I) [8]

Hexatriene **I** was added dropwise to a heated 50 ml flask, evaporated and transferred in a stream of nitrogen into a quartz tube (3 cm i.d., 30 cm length) and heated in an electric oven. The reaction was monitored by GLC methods (dinonyl phthalate, 60 °C). The crude product was collected in a receiving flask cooled in a Dry Ice/ethanol mixture. The reaction conditions employed are listed in Table 1.

TABLE 1

Conditions for the thermal isomerization reaction of I

Temperature (°C)	Reaction time (s)	Input (g)	Conversion (%)
400	5.7	7.0	78
450	6.5	20.0	80
500	17.2	9.6	60

Octafluoro-1,3-cyclohexadiene (IV) [15]: IR (cm^{-1}): 980 (s); 990 (vs); 1095 (vs); 1165 (m); 1250 (m); 1270 (s); 1320 (m); 1330 (s); 1350 (vs); 1400 (vs). MS *m/z* (%): 31/13 (CF^+); 50/18 ($CF_2{}^+$); 69/21 ($CF_3{}^+$); 93/17 ($C_3F_3{}^+$); 124/43 ($C_6F_4{}^+$); 155/100 ($C_5F_5{}^+$); 174/38 ($C_5F_6{}^+$); 205/38 ($C_6F_7{}^+$); 224/54 (M^+). ^{19}F NMR δ: 124.15 (4F, m, $-CF_2-$); 151.47 (2F, m, $-CF=$); 161.29 (2F, m, $=CF-$) ppm.

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