CYCLODIMERIZATION OF PERFLUORO-2-METHYLENE-4-METHYL-1, 3-DIOXOLANE

V. S. Yuminov, S. V. Kartsov, V. L. Maksimov, O. A. Popova, and K. M. Makarov

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One of the most characteristic properties of fluoroolefins is their capacity to undergo two-step biradical [2 + 2]-cycloaddition [1].

We are the first to report such a reaction for perfluoroketeneacetals. Specifically, cyclodimer (II) was obtained from perfluoro-2-methylene-4-methyl-1,3-dioxolane (I) at 150°C in the presence of diglyme* in 90% yield.



The unexpected ease[†] and regiospecificity of the cyclodimerization of perfluoroalkene (I) are a consequence of the formation of biradical (A) as an intermediate, in which each radical site is stabilized by two oxygen atoms.

Mass and ¹³C NMR spectral data were used to select between 1,2- (II) and 1,3-disubstituted cyclobutanes (III).

The mass spectrum shows a molecular ion peak and the characteristic decomposition of this peak for cyclobutanes by two pathways [3]: a) "symmetrical" decomposition with the loss of molecule (I) and formation of strong m/z 244 ions and b) decomposition with the loss of perfluoroethylene or tetraoxafulvalene



Decomposition pathway b cannot be realized in the case of 1,3-structure (III).

The ¹³C NMR spectrum has a triplet of triplets at 113 ppm with couplings of 302 and 25 Hz due to the interaction of ¹³C nuclei with the ¹⁸F nuclei at the α and β positions, respectively [4] (Table 1), which corresponds to a CF_2 -CF₂ fragment.

^{*}Diglyme was used as an inhibitor of the radical homopolymerization of perfluoroalkene (I). [†]The only reported example for perfluoroalkyl vinyl ethers is the cyclodimerization of perfluoro-1,2-di(vinyloxy)ethane under extremely vigorous conditions (at 135°C and 5000 atm) [2].

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TABLE 1. $^{13}\mathrm{C}$ and $^{19}\mathrm{F}$ NMR Spectral Characteristics of Cyclodimer (II)

Group	Dei			19F
	ð, ppm*	J, Hz	²J, Hz	ð. ppm**
$CF_2 CO_2 CF_2 O CF CF_3 CF_3 CF_3 CF_3 CF_3 CF_3 CF_3 C$	113,2 107,4 123,3 105,1 117,8	302t - 282 t 263 d 284 q	25 t 26 t 28 d 42 q , 42 d, 29 d 38 d	55,1-56,4m 2,0-5,6 m 10,0-13,4m 49,4-51,3 m 3,6-4,5 m

*Relative to external HMDS.

**Relative to external CF_3CO_2H (upfield signals are indicated by a plus sign).

The CF_3 group in the dioxolane ring in alkene (I) accounts for the formation of regioand stereoisomers as a result of the cyclodimerization of this compound, which is evident in the complex structure of the ¹⁹F NMR spectrum of the product.

EXPERIMENTAL

The mass spectrum was taken on a Varian MAT CH-8 mass spectrometer at 70 eV. The NMR spectra were taken on a Bruker WP-200 spectrometer at 50.3 MHz for the 13 C NMR spectra and 188.3 MHz for the 19 F NMR spectra.

<u>Perfluoro-2-methylene-4-methyl-1,3-dioxolane (I)</u>. A sample of 100 g dry Na_2CO_3 and 140 g absolute diglyme was added to a three-necked flask equipped with a stirrer, thermometer, dropping funnel, and gas outlet tube connected to a coiled cooled trap maintained at -78°C. Then, 136 g perfluoro-2,4-dimethyl-2-fluorocarbonyl-1,3-dioxolane was added [5]. The reaction mixture was stirred for 3 h and then warmed to 135°C. The products were distilled to give 43 g (40%) dioxolane (I), bp 44.5-45.0°C (44.8°C [5]).

 $\begin{array}{l} \underline{\operatorname{Perfluoro-2,8(9)-dimethyl-1,4,7,10-tetraoxadispiro[4.0.4.2]dodecane (II).} \quad A \mbox{ mixture of 50 g dioxolane (I) and 0.5 g absolute diglyme was placed into a steel autoclave and maintained in a rocking furnace for 4 h at 150°C and then distilled to give 45 g (90%) colorless cyclodimer (II), bp 126.0-126.5°C, d_20⁴ 1.74. Found, %: C 24.63, F 62.45. C_{10}H_{16}O_4. Calculated, %: C 24.61, F 62.28. Mass spectrum, m/z (relative intensity, %): M⁺ 488(3.3), [M - F]⁺ 469(4.2), [M - COF]⁺ 441 (12.6), [M - CF_3]⁺ 419(8.2), [M - C_2F_4]⁺ 388(12.2), [C_6F_9O_2]⁺ 275-(46.8), [M/2]⁺ 244(81.8), [C_5F_7O_2]⁺ 225(6.3), [C_4F_7O_2]⁺ 213(4.3), [C_4F_5O]⁺ 159(4.3), [C_3F_6]⁺ 150(100), [C_3F_5O]⁺ 147(11.8), [C_3F_5]⁺ 131(8.4), [C_3F_4O]⁺ 128(6.6), [C_2F_5]⁺ 119(7.9), [C_3F_4]⁺ 112(11.0), [C_3F_3O]⁺ 109(18.5), [C_2F_4]⁺ 100(48.6), [C_2F_3O]⁺ 97(13.1), [C_3F_2O]⁺ 90(9.5), [C_2-F_2O]⁺ 78(44.9), [CH_3]⁺ 69(39.3). \end{array}$

CONCLUSIONS

The thermal head-to-head cyclodimerization of perfluoro-2-methylene-4-methyl-1,3-dioxolane was carried out.

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