POLAR ADDITION OF PERFLUORO-TERT-HEXYL IODIDE TO ALKENES AND ALKYNES

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The effective charges on the atoms in molecules of perfluoroalkyl halides of general formula $(CF_3)_n CF_{3-n}X$ (X = Cl, Br, I) have been calculated by the AM1 semiempirical method. In polar solvents perfluoro-tert-hexyl iodide is reduced under the action of alkenes, and aromatic hydrocarbons to form 2-hydroperfluoro-2-methylpentane and perfluoro-2-methyl-2-pentene. In ethyl acetate the regio- and stereospecific addition of perfluoro-tert-hexyl iodide to alkenes, butadiene, and alkynes takes place, which is associated with the realization of a polar ion-radical mechanism for the reaction.

The homolytic addition of perfluoroalkyl iodides R_FI at a carbon-carbon multiple bond is achieved at elevated temperatures (180-220°C), in the photolysis of the C-I bond, or in the presence of radical initiators [1]. However, in polar solvents addition at the multiple ICl bond is brought about by an ionic, electrophilic mechanism [2]. Taking the high electronegativity of the perfluoroalkyl group into account it can be postulated that the polarization of the C-I bond in R_FI leads to the formation of a partial positive charge at the iodine atom. In such a case the addition of R_FI at a multiple bond in a similar way to the addition of iodine chloride becomes probable.

To determine the charge at the halide atom in perfluoroalkyl halides of various structures we have conducted quantum chemical calculations of these molecules by the AM1 semiempirical method. The values obtained for the effective charges at just the carbon atoms of the C-X bond (Q_{C-X}) and the halogen X (Q_X) are presented in Table 1. The complete results of the calculations will be published later. All the effective charges by the AM1 method are obtained in the Mulliken approximation [3].

It follows from the data in Table 1 that both a decrease in the electronegativity of the halide (Cl \rightarrow Br \rightarrow I) and an increase in the electronegativity of the perfluoroalkyl group (from the primary to the secondary and even more to the tertiary) are accompanied by the appearance of an effective positive charge at the halide atom. In the case of perfluoro-tert-butyl iodide an appreciable positive effective charge (+0.252) is formed at the iodine atom.

	X=	= Cl	X=	Br	X=I		
R _F	Q _{C-CI} Q _{CI}		Q _{C-Br}	Q _{Br}	Q _{C-I} Q _I		
CF ₃ CF ₃ CF ₂ (CF ₃) ₂ CF (CF ₃) ₃ C	0,443 0,260 0,046 -0,205	-0,044 -0,032 0,009 0,062	0,365 0,182 -0,042 -0,305	0,043 0,053 0,093 0,147	0,275 0,095 -0,130 -0,396	0,164 0,170 0,206 0,252	

TABLE 1. Effective Charges (calculated by the AM1 method) at the Carbon $({\rm Q}_{C-X})$ and the Halide $({\rm Q}_X)$ Atoms in Perfluoro-alkyl Halides R_FX

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Substance	Meth-	Yield, %	Bp, °C (p, mm Ha)	Mass spectrum	IR spec- trum	Found Calcu %	/ lated
	<u> </u>		(1 <u>6</u>)		cm ⁻¹	С	H
R _F CH ₂ CH ₂ I	B	73,1	84 (55)	474(M+; 41,8%)		19,79	0.89
R _F CH ₂ CHICH ₃	B	82,4	74(25)	$347(M^+ - I; 5.5\%)$ $361(M^+ - I; 100\%)$		20,25 22,15	0,84 1,25
BrCH,CHIC,H	A	84.0	88(7)	$403(M^+ - 1; 100\%)$		22,13 26,96	1,23 2.08
B-CH-CHIC-H.	À	76.4	96(7)	$417(M^+ - I: 44.7\%)$		27,17 28.63	2,26
		10,4	00(1)			28,68	2,57
R _F CH ₂ CHICH ₂ OCOCH ₃	A	44,7	98(10)	$419(M^+ - I; 100\%)$		24.08	$\frac{1.71}{1.47}$
$R_FCH = CHI$	В	85,4	80(70)	472(M+; 100%)	1610	20,27	0,41
B-CH=CIC.H	А	91.8	102(7)	548(M+: 0.9%)	1633	20,34 30.66	0,42
the an - or office		01,0	10-(17	$421(M^+ - I; 100\%)$		30,66	1,09
$R_FCH = CICH_2OCOCH_3$	A	87,2	86 (8)	$485(M^+ - AcO; 2.2\%),$	1634	24.08	1.10
			05 (0)	$417(M^+ - 1; 100\%)$	1005	24.26	1,10
$R_FCH_2 = CHCH_2I$	В	91,5	č5(9)	$500(M^+; 0.4\%),$ $373(M^+ - I: 100\%)$	1005	24.00	1,10
R _F CH=CHC ₄ H ₂		88,3	166 (760)	402(M+; 9,4%)	1667	35.55	2,71
	1					35.82	2.74

TABLE 2. Products from the Addition of R_FI to Alkenes and Alkynes $[R_F = C_3F_7C(CF_3)_2]$

It is evident that the existence of such an appreciable charge at the iodine atoms in tertiary perfluoroalkyl iodides may have a substantial effect on the energetics of the transition state in the reaction of $(R_F)_3CI$ with a π -system. Such an effect should be exhibited to the greatest extent in polar organic solvents. In this connection we studied the reaction of perfluoro-tert-hexyl iodide (I) with 1-heptene in DMF. Here (I) is unexpectedly converted completely into perfluoro-2-methyl-2-pentene (II) and 2-H-perfluoro-2methylpentane (III) at 80°C, which undoubtedly indicates the intermediate formation of the perfluoro-tert-hexyl anion. It should be noted that (I) reacts neither with heptene (without a solvent) nor with DMF (80°C, 3h). Such a direction for the process would seem to be the result of electron transfer from heptene to the iodide (I) in a polar medium to form an intermediate anion radical (IV), which dissociated in DMF to the perfluoro carbanion (V) and atomic iodine. The formation of (II) and (III) is the result respectively of the elimination of F⁻ or proton capture from the solvent



We showed by polarography at platinum that (I) is a stronger oxidant than I_2 : the reduction potential of (I) at Pt in CH₃CN is 0.32 V (relative to the SCE), whereas for I_2 under the same conditions E = 0.10 V (SCE). We note that the potentials for the oneelectron oxidation of alkenes (at Pt in CH₃CN) to the corresponding cation radicals occur in the far positive region, above 2.8 V (SCE) [4]. When evaluating a process such as the oxidation of 1-heptene by a perfluoroalkyl iodide, which seems unlikely at first glance, it should be taken into account that electron transfer for $(R_F)_3$ CI has an irreversible nature due to the dissociative rupture of the C-I bond. Such a homogeneous transfer of

ABLE 3. PMR Spec	ctrum of Con	npounds Obt;	ained				I			
2 4 3 1		PMR (δ, ppu	n, cc1 ₄)				¹⁹ F NMR	r (ô, 1	opm, C(31 ⁴)
(.F _a (.F ₂ (.F ₂ (.F ₃) ₂)?		2	ę	4	5	J, Hz	1	67	en	4
°CI12CI121	3,14 t (2H)	2,60 t (2H)				(1-2)8,5	-14,7 (6F)	2,4 (3F)	29,7 (2F)	45,9 (2F)
2 1 3 FCII2CHICH3	4,33 d.d.q (111)	A, 2,98 d.d B, 2,59 d.d (211)	1,84 d (3H)			$(1-2\Lambda)2, (1-2B)6,5, (1-3)6,5, (2\Lambda B)16,5$	-15,1 (6F)	2,5 (3F)	29,2 (2F)	45,7 (2F)
² ¹ ³ ⁴ ⁵ ⁵ ⁵ ⁵ ⁵	4,09 m (111)	A, 2,98 d.d B, 2,65 d.d (211)	A. 1,59 d.d.t B, 1,38 d.d.t (2H)	1,03-1,29 m (<i>A</i> H)	0,74 t (3H)	(1-2A)2,5, (1-2B)5, (1-3A)5,5, (1-3B)2, (2AB)16,5, (3AB)12,5	-15,3 (6F)	2,4 (3F)	29,3 (2F)	45,8 (2F)
2 1 3 4 5 FCII2GIIICII2(CII2)3CII3	4,22 m (111)	A, 3,06 d.d B, 2,74 d.d (211)	A, 1,67 d.d.t B, 1,77 d.d.t (211)	t,09–t,56 m (611)	0,79t (311)	(1-2A)2, (1-2B)5,5, (1-3A)5, (1-3B)2,5, (2AB)17, (2AB)11	15,6 (6F)	2.7 (3F)	29, t (2F)	45,5 (2F)
³ 1 2 4 cH2CH2CCH3	4,29 d.d.d.d (111)	A, 4,10 d.d B, 3,94d.d (211)	A, 2,97 d.d B, 2,73 d.d (2H)	1,84 s. (3H)		(1-2A)5,5,(1-2B)6,5 (1-3A)4,5,(1-3B)5,(2AB)12,(3AB)12	-16,1 -15,1 (6F)	2,4 (3F)	28,4 (2F)	45,3 (2F)
cH=CHI	(111) 0'2	6,37 d (111)				(1-2) 15	-14,6 (6F)	3.0 (3F)	31.6 (2F)	46.2 (2F)
² ¹ FCII → CIC ₆ II ₅	6,98m (511)	6,4 1s (111)					16,4 (6F)	2,4 (3F)	30,9 (2F)	46,4 (2F)
¹ ² ³ ³ ⁴ CII=CICH ₂ OCOCH ₃	6,42s (111)	4,57s (2H)	1,95 _S (3H)				-15,3 (6F)	2,4 (3F)	30,7 (2F)	45,8 (2F)
4 2 1 3 FCH_CH_CHCH2I	5,84 t (III)	5,56 d.t (111)	3,68d (211)	2,84 d (211)		(1-2) 14,5, $(1-3)$ 7,5, (2-4) 6,5	-14,3 (6F)	2,3 (3F)	29,3 (2F)	45,4 (2F)
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an electron "against the potential" has been noted previously in the reduction of the C-Cl bond by means of an electrochemically generated "electron carrier," e.g., the anion radical of nitrobenzene [5].

It was found that in DMF perfluoro-tert-hexyl iodide is capable of electron transfer from the molecule of hydroquinone and even benzene: in both cases heating at 80°C in DMF leads to the formation of the perfluoroolefin (II) and the monohydroperfluoroalkane (III). Furthermore, the addition to (I) of a readily oxidizable olefin, ethyl vinyl ether, leads to the appearance of the perfluoroolefin (II) even in a less polar solvent, ethyl acetate at 20°C.

Contact under these conditions with olefins which are difficult to oxidize does not lead to the deiodofluorination of (I). However, on heating (I) to 80°C in ethyl acetate a smooth regio- and stereospecific addition to ethylene and monosubstituted alkenes, 1,3butadiene, acetylene, and monosubstituted acetylenes takes place



 $R_F=C\;(CF_3)_2C_3F_7;\;R=H,\;CH_3,\;C_4H_9,\;C_5H_{11},\;CH_2OCOCH_3;\;R'=Ph,\;CH_2OAc.$

High regio- and stereospecificity are not characteristic of radical processes, which gives reason to suggest a polar ion-radical addition mechanism for the reaction of (I) with olefins and acetylenes.

EXPERIMENTAL

PMR spectra were obtained on a Bruker R-200-SY spectrometer (200 MHz), the ¹⁹F NMR spectra on a Bruker R-32 spectrometer (84.6 MHz), using TMS and CF₃COOH as external standards, the mass spectra on a Varian MAT-CH-8 spectrometer, and the IR spectra on a UR-20 spectrometer.

Addition of (I) to Alkenes and Alkynes. Method A. A mixture of 20 mmoles of (I) and 20 mmoles of the unsaturated compound in 15 ml ethyl acetate was heated for 4-5 h at 70-80°C with a reflux condenser, the solvent was removed under vacuum, and the residue washed with $Na_2S_2O_3$ solution and water, dried with MgSO₄ and distilled under vacuum.

<u>Method B.</u> A mixture of 20 mmoles of (I) and 25 mmoles of the unsaturated compound in 15 ml of ethyl acetate was heated for 5-6 h at 80-90°C in a 60-ml steel autoclave having a Teflon inset; the reaction mixture was cooled and treated as in method A.

<u>Dehydroiodination of the Addition Products</u>. 10 mmoles (VI, $R = C_4H_9$) and 12 mmoles of EtONa in 10 ml of ethanol were boiled for 0.5 h, cooled, and diluted with 30 ml of water. The lower layer was separated off, washed with 10% HCl, then water, and dried with MgSO₄. Trans-1,1,1,2,2,3,3-heptafluoro-4,4-bis(trifluoromethyl)-5-decene was separated by distillation.

The experimental, physicochemical, spectral, and analytical data are presented in Tables 1-3.

LITERATURE CITED

- 1. W. A. Sheppard and C. M. Sharts, Organic Fluorine Chemistry, W. A. Benjamin, New York (1969).
- 2. C. K. Ingold, Structure and Mechanism in Organic Chemistry, 2nd ed., Cornell Univ. Press, Ithaca (1969).
- M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. P. Stewart, J. Am. Chem. Soc., <u>107</u>, 3902 (1985).

4. I. N. Rozhkov, Usp. Khim., <u>45</u>, 1222 (1976).

5. H. Lund, M. Michel, and J. Simonett, Acta. Chem. Scand., <u>B28</u>, 900 (1974).

METHYLENECYCLOPROPANE IN THE [2+2+1]-CYCLOADDITION REACTION WITH DICOBALT-HEXACARBONYL COMPLEXES OF ACETYLENES*

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The ability of methylenecyclopropane to undergo [2+2+1]-cycloaddition reactions with dicobalt-hexacarbonyl complexes of alkynes with formation of spiro[2,4]heptenone derivatives has been revealed for the first time. The conditions for carrying out this reaction on the surface of adsorbents and zeolites have been established, so that it can be considered as a general preparative method for the preparation of various derivatives of spiro[2,4]heptenones (yields up to 80%). With monosubstituted acetylenes, the [2+2+1]-cycloaddition proceeds regioselectively, giving preferentially cyclopentenones containing a spiro fragment in the β -position to the carbonyl. In the case of disubstituted acetylenes, α -isomers are formed exclusively.

In the reaction of dicobalt-hexacarbonyl complexes (DCHCC) of acetylenes with alkenes, a [2+2+1]-cycloaddition takes place with the formation of cyclopentenones (the Khand-Pauson reaction [2]). This reaction is particularly effective in the case of olefins with a strained double bond (norbornene, cyclobutene) [3]. The strained character of the double bond in methylenecyclopropane (I) is clearly manifested in its high activity in the [4+2]-, [3+2]and [2+2]-cycloaddition reactions [4]. At the same time, (I) is also characterized by its ability to react with ring opening and intermediate formation of a trimethylenemethane biradical. Processes of this type proceed particularly readily in the presence of transition metal complexes, for example of Ni (0) [4].

The aim of the present work was to investigate the possibility of using (I) in the Khand-Pauson reaction. This reaction is usually carried out by prolonged heating of the mixed reagents in hydrocarbon solvents at 60-100°C [2]. However, in the case of (I), the reaction of methylacetylene (IIa) with DCHCC) in hexane medium proceeds even at 20-40°C, whereby, after a certain induction period (\sim 2 h), heating up and considerable resinification of the reaction mixture is observed. The yield of [2+2+1]-cycloaddition products, 6-methyl-spiro[2,4]hept-6-en-5-one (IIIa) and 5-methyl-spiro[2,4]hept-5-en-4-one (IVa) (\sim 1:1), did not exceed 14% with a total conversion of (IIa). In addition to these products, 1-cyclopropylidenepent-3-ene-2-one (Va) is also formed (yield 7%).+ Despite the high activity of of (I) as an olefin component in the Khand-Pauson reaction,‡ the low yield of the corresponding cyclopentenones necessitated development of an alternate method of carrying them out.

*For previous communication; see [1].

†In general terms, this reaction corresponds to hydrocarbonylation of the triple bond with the subsequent reaction of the acyl-cobalt intermediate with olefinic component. There are data in the literature on the possibility of the formation of such dienones by the Khand-Pauson cyclization, which is probably due to their lability under the more rigorous conditions of carrying out the reaction. #For comparison, we shall note that with such an active olefin as cyclobutene, this reaction is carried out under more rigid conditions (60-80°C, 4-6 h) [3].

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