Russian Journal of General Chemistry, Vol. 75, No. 7, 2005, pp. 1136–1138. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 7, 2005, pp. 1199–1201.
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Reaction of Perfluorocarbonyl Chlorides with Ethyl- and Phenylmagnesium Bromides

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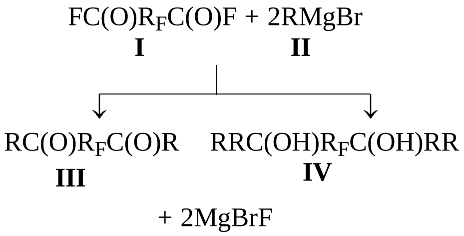
Received March 23, 2004

Abstract — The structure of the products formed by the reactions of perfluoroadipoyl and perfluorocyclohexanedicarbonyl difluorides with ethyl- and phenylmagnesium bromides depends on the nature of the radical in the organomagnesium compound.

Polyfluorinated diketones are applied as extractants, monomers, biologically active compounds, and synthetic intermediates [1]. Polyfluorinated ketones have been prepared by organomagnesium synthesis [2–4], but reactions of perfluorocarbonyl fluorides with Grignard reagents have scarcely been reported.

Here we present the synthesis of polyfluorinated diketones by the reactions of perfluoroadipoyl and perfluorocyclohexanedicarbonyl difluorides with ethyl- and phenylmagnesium bromides.

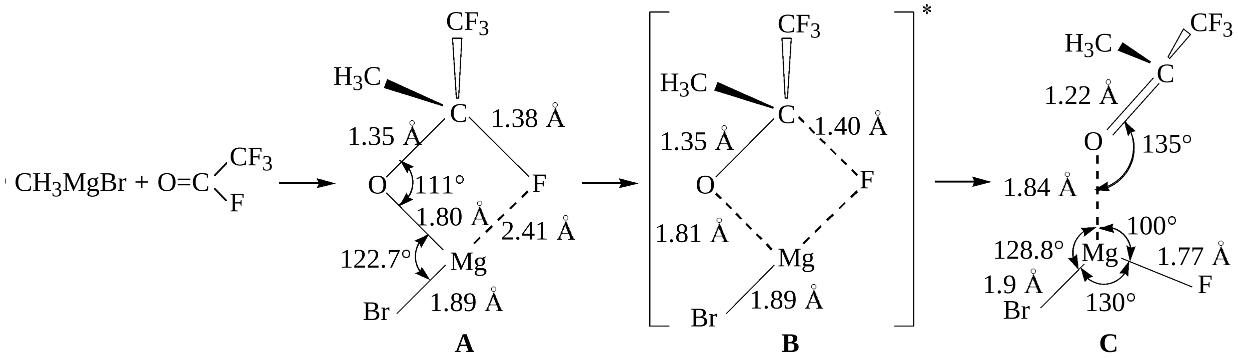


$R_F = (CF_2)_4, C_6F_{10}; R = Et, Ph.$

The yield of the diketones is much dependent on the structure of both the starting difluoride and the radical in the organomagnesium reagent. On replacement of phenyl by ethyl in the Grignard reagent the yield of the diketone decreases from 62% with compound **IIIb** to 15% with compound **IIIa**, whereas in going from the perfluroalkyl- to perfluorocyclohexyl-containing difluoride, the reaction yield decreases from 62% with compound **IIIb** to 21% with compound **IIId**. The properties of the synthesized compounds are presented in the table.

With excess Grignard reagent, as well as at temperatures above –15°C, reactions leading to tertiary alcohols take place. The formation of tertiary alcohols in reactions of organometallic compounds with perfluorocarboxylic acid derivatives is explained [5] by the fact that increased temperature induce reaction of the resulting carbonyl compounds with new molecules of the Grignard reagent. Bulky radicals prevent formation of tertiary alcohols. Therefore, no tertiary alcohols were detected by GLC in the reaction of perfluorocyclohexanedicarbonyl difluoride with phenylmagnesium bromide.

To gain insight into the mechanism of the reaction in hand, we calculated its elementary stages by MNDO–PM3 [6–8] with full geometry optimization. As model compounds we chose methylmagnesium bromide and perfluoroacetyl fluoride (see scheme). According to the calculations, first an adduct of



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Constants, yields, melting and boiling points, IR and ^{1}H NMR spectra, and elemental analyses of fluorinated diketones $RC(O)R_FC(O)R$

Comp. no.	Yield, %	mp, °C or bp, °C (p, mm Hg)	d_4^{20}	n_D^{20}	IR spectrum, ν, cm^{-1}		^{1}H NMR spectrum, δ, ppm	Found, %			Formula	Calculated, %		
					C=O	OH		C	H	F		C	H	F
IIIa	15	64 (5)	1.4332	1.3671	1750	3365	1.02 t (3H, Me), 2.93 q (2H, CH_2), 4.48 m (1H, CH), 12.90 s (1H, OH)	37.46	3.24	48.01	$C_{10}H_{10}F_8O_2$	38.22	3.18	48.41
IIIb	62	42–43	–	–	1760		7.43–8.15m (5H, C_6H_5)	52.15	2.48	36.90	$C_{18}H_{10}F_8O_2$	52.68	2.44	37.07
IIIc	16	85 (7)	1.5483	1.3602	1765	3380	1.12 t (3H, CH_3), 2.95 q (2H, CH_2), 4.52 m (1H, CH), 13.10 s (1H, OH)	37.72	2.79	50.12	$C_{12}H_{10}F_{10}O_2$	38.30	2.66	50.53
IIId	21	155–156	–	–	1770		7.69–8.14 m (5H, C_6H_5)	49.83	2.16	39.81	$C_{20}H_{10}F_{10}O_2$	50.85	2.12	40.25

CH_3MgBr adds to perfluorinated acyl fluoride. The energy of adduct formation is ~10 kJ mol^{-1}, and its the most stable structure comprises a four-membered ring **A** with C–F, C–O, and Mg–O bonds lying in the same plane. Further on structure **A** undergoes rearrangement via transition state[1] **B** with a barrier (activation energy) of about 30 kJ mol^{-1} into complex **C** (see figure). The geometric parameters of all the mentioned structures are given in the scheme. As seen from the scheme, structure **A** converts into complex **C** via synchronous stretching of the C–F and O–Mg bonds.

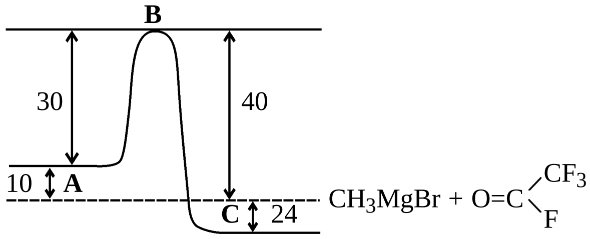
EXPERIMENTAL

The IR spectra were obtained on a Specord IR-75 spectrophotometer (NaCl prysm, 4000?600 cm–1) in thin films for liquids and mulls in mineral oil for solids. The NMR spectra were obtained on a Bruker-300 spectrometer (300 MHz), internal standards TMS and DMSO-d_6.

Gas chromatography was performed on an LKhM-8MD chromatograph using columns (3 × 3000 mm) packed with 10% SKTFT on Chromosorb-W.

Perfluoroadipoyl and perfluorocyclohexanedicarbonyl difluorides, bromobenzene, and bromoethane were commercial products. Ether was distilled over P_2O_5 and handled over sodium. Ethyl- and phenylmegnesium bromides were prepared by the procedure in [5].

Fluorinated diketones *(general procedure).* A solution of 0.02 mol of alkyl- or arylmagnesium bromide in 20 ml of absolute ether was added dropwise to a solution of 0.002 mol of perfluorocarbonyl difluoride in 25 ml of the same solvent cooled to –15°C. The reaction mixture was allowed to stand for 1 h at –15 to –10°C, after which it was let to warm to room temperature. After standing for an additional 3 h, the mixture was refluxed for 0.5 h and then treated with 10% HCl. Organic compounds were extracted with ether, and the extract was washed with 1% potassium carbonate to neutral washings and dried



Energy diagram of the reaction of perfluoroacetyl fluoride with methylmagnesium bromide as given by the quantum-chemical calculations (activation energies are in kJ mol^{-1}).

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[1] Transition state was found by automatic search for the corresponding node point on the potential energy surface as a function of all geometric parameters.

with calcium chloride. The solvent was removed, and liquid reaction products were purified by repeated vacuum distillations and solid, by recrystallization from chloroform.

REFERENCES

1. Ishikawa, N. and Kobayashi, E., *Fluorine Compounds*, Tokyo: Kodansha Scientific, 1982.
2. Dormidontov Yu.P., Kazakov Yu.P., Shchadrina L.P., Simonov, A.R., and Ponomarev, V.G., *Zh. Org. Khim.*, 1990, vol. 26, no. 3, p. 533.
3. Chen, L.S., Chen, G.J., and Tamborski, C., *J. Fluorine Chem.*, 1984, vol. 26, no. 3, p. 341.
4. Chen, L.S., Fratini, A.V., and Tamborski, C., *J. Fluorine Chem.*, 1986, vol. 30, no. 3, p. 381.
5. Batizat, D.V., Yarosh, A.A., Ignatenko, A.V., and Ponomarenko, V.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, no. 5, p. 1163.
6. Dewar, M.J.S. and Thiel, W., *Theor. Chim. Acta*, 1977, vol. 46, p. 89.
7. Dewar, M.J.S. and Thiel, W., *J. Am. Chem. Soc.*, 1977, vol. 99, no. 15, p. 4899.
8. Stewart, J.J.P., *J. Comput. Chem.*, 1989, vol. 10, no. 2, p. 209.