Journal of Fluorine Chemistry, *47* (1990) 435–440

Received: March 8, 1989, accepted: January 30, 1990

SYNTHESIS OF 1-ADAMANTANOL 2,3,3-TRIFLUOROACRYLATE

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SUMMARY

1-Adamantanol 2,3,3-trifluoroacrylate (4), i.e. (tricyclo-[3,3,1,$1^{3,7}$]dec-1-yl) 2,3,3-trifluoro-2-propenoate, was synthesized on the basis of freons as a new potential monomer.

INTRODUCTION

The highly symmetrical structure of the adamantane skeleton often imparts unusual properties to compounds and materials that contain this rigid hydrocarbon moiety. For that reason, adamantane derivatives have been increasingly employed in polymers, because of their high thermal stability, high glass-transition temperature, low crystallinity and good hydrolytic stability [1,2]. Polymeric methacrylates of adamantanols exhibit excellent optical properties, low mold shrinkage, and have been used recently for optical-fibre core materials [3-6].

On the other hand, esters of 2,3,3-trifluoroacrylic acid have also given a possibility of preparing copolymers with

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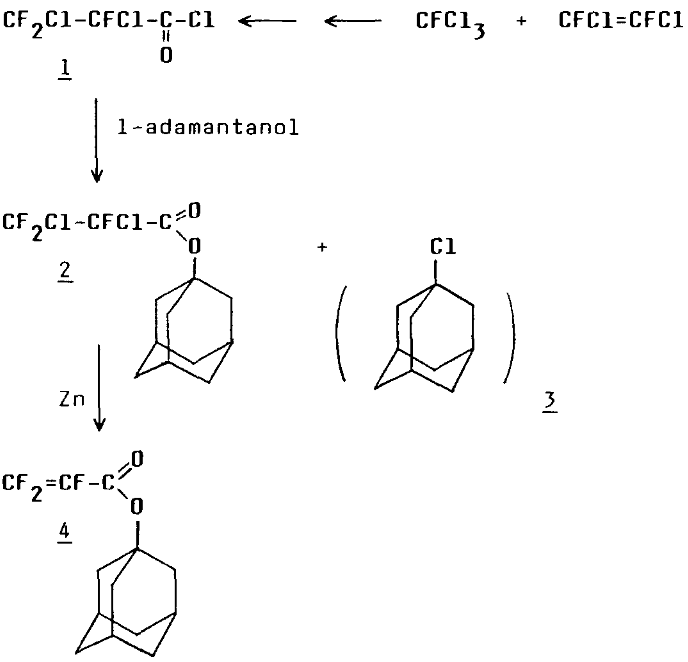
important properties [7]. On the basis of these facts we have supposed that a polymer formed from a monomer, containing both the adamantane core and fluorinated double bond, e.g. adamantanol trifluoroacrylate, could also possess interesting properties.

RESULTS

The starting compounds for the synthesis of 1-adamantanol 2,3,3-trifluoroacrylate (4) used were 2,3-dichloro-2,3,3-trifluoropropanoyl chloride (1) and 1-adamantanol (tricyclo[3,3,1,$1^{3,7}$]decan-1-ol). Preparation of acid chloride 1 can be easily performed by our method on a large scale [8,9] from trichlorofluoromethane and 1,2-dichlorodifluoroethylene. The reported reaction of methacryloyl chloride with 1-adamantanol yielded the corresponding ester in a very low yield [10]; better yields of 1-adamantanol methacrylate were obtained by the reaction of silver methacrylate with 1-bromoadamantane [11]. In our case, acylation of 1-adamantanol with acid chloride 1



in a benzene solution was unsuccessful and the only product isolated was 1-chloroadamantane (3, yield 6-9 %). The desired 1-adamantanol 2,3-dichloro-2,3,3-trifluoropropanoate (2) was prepared in yields of 67-78 % by carrying out the reaction in the presence of pyridine or triethyl amine. 1-Chloroadamantane was formed as a by-product in a relative amount of 10-15 % [12].

The last step in the synthesis of monomer 4 was dehalogenation of ester 2 with activated zinc in 1,2-dimethoxyethane. We had used a similar method for the preparation of ethylene glycol bis-trifluoroacrylate [13]. The conversion of the starting ester 2 exceeded 95 %, and the preparative yields achieved were 69-76 %. The structure of the compounds 2 and 4 was verified by elemental analysis and spectra (^{19}F NMR, MS and IR).

EXPERIMENTAL

General comments and apparatus

All boiling points are uncorrected. The GLC analyses were performed on a Chrom 41 instrument (see Ref. [1]), stationary phase poly(1,4-butanediol succinate). The preparative GLC was performed on a modified Chrom 2 instrument (FID with a by-pass, 500-cm column with 1-cm diameter).

The IR spectra were recorded on a Perkin-Elmer instrument (Bodenseewerk, cm^{-1}; w - weak, m - medium, s - strong absorption). The NMR spectra were recorded on a Varian XL 100/15 instrument (100 MHz, CW; deuteriochloroform and dimethyl sulphoxide-d_6 as solvents, tetramethylsilane and $CFCl_3$ as internal standards, chemical shifts in ppm, coupling constants J in Hz). The mass spectra were scanned on a GLC - Mass Spectrometer tandem LKB 9000 (single focus; helium, GLC inlet via a column 0.23x250 cm packed with OV-210 on Chromaton N-AW).

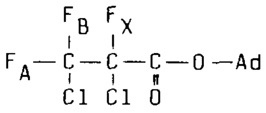
Chemicals and compounds used

1-Adamantanol was prepared by the described method [14]. 2,3-Dichloro-2,3,3-trifluoropropanoyl chloride (1) was prepared according to the described procedure [8,9]. 1,1,2-Trichloro-1,2,2-trifluoroethane (Ledon 113 was supplied by

Spolek pro chemickou a hutní výrobu, Ústí n.L.); 1,2-dimethoxy ethane was purified and dried by general methods.

1-Adamantanol 2,3-dichloro-2,3,3-trifluoropropanoate (2)

In a typical run, acid chloride 1 (37.8 g, 0.176 mol) in a benzene solution (1:1 v/v) was added dropwise at 90 °C (oil bath) during 1 h to a stirred mixture of 1-adamantanol (24.3 g, 0.160 mol), benzene (200 ml) and pyridine (13.9 g, 0.176 mol). After stirring and heating 1 h at 90-100 °C, the crystal line phase was filtered off and the benzene solution was evaporated on a rotatory evaporator. The residual raw product was distilled under the reduced pressure and a fraction of b.p. 90-98/9.4 (°C/Pa) was obtained with a content of *ca.* 74 % (GLC) of product 2, which corresponded to a yield of *ca.* 37 g (70.2 %). Admixtures of 1-adamantanol and 1-chloroadamantane in product 2 were taken off by fractional sublimation at 80-90 /2.6 (°C/kPa), and the purity of compound 2 exceeded 96 % after refining. 1-Chloroadamantane was identified by comparing its mass spectrum with that of an authentic sample. IR spectrum of compound 2 (carbon sulphide, tetrachloromethane): 705 m, 794 m, 824 ms, 848 s, 937 m, 961 m, 1 044 s, 1 067 m, 1 101 m, 1 146 s, 1 156 s, 1 213 ms, 1 268 vs, 1 310 m, 1 321 m, 1 355 m, 1 456 m, 1 769 vs, 2 861 ms, 2 920 s. For $C_{13}H_{15}Cl_2F_3O$ (332.2) calculated/found: 47.1/47.2 %C, 4.6/4.8 %H, 21.4/21.6 %Cl, 17.2/17.0 %F.
^{19}F NMR spectrum (dd - doublet of doublets):



$F_A-\underset{Cl}{\overset{F_B}{C}}-\underset{Cl}{\overset{F_X}{C}}-\underset{\overset{\|}{O}}{C}-O-Ad$

F_A: dd -63.8, $^2J_{AB}$ 168, $^3J_{AX}$ 7
F_B: dd -66.8, $^3J_{BX}$ 11
F_X: dd -124.8

1-Adamantanol 2,3,3-trifluoroacrylate (4)

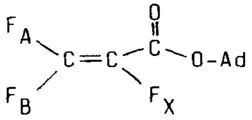
In a typical run, zinc powder (3 g, 46 mmol) was activated with iodine (0.15 g) by heating at 130-150 °C and stirring for 15 min. in a reaction flask. A solution of halogenopropanoate 2 (9.92 g, 30 mmol) in 1,2-dimethoxyethane (40 ml) was added dropwise during 30 min. to the activated zinc under heating to keep the mixture refluxing. The conversion of the starting compound 2 exceeded 95 % after 4 h. Ledon 113 (100 ml) and magnesium sulphate powder were then added to the mixture which was then filtered and the solvent mixture was distilled off; the residue (ca. 6.5 g) contained raw trifluoroacrylate 4. Raw products of two runs were combined and rectified on a packed column under reduced pressure; the main fraction of b.p. 72-75/7.3 (°C/Pa) was obtained in a corresponding mean yield 5.62 g (72.1 %), purity 93 %. For analytical purposes product 4 was re-rectified in the same manner.

IR spectrum (tetrachloromethane): 844 m, 963 mw, 1 046 m, 1 081 s, 1 203 s, 1 297 s, 1 308 m, 1 317 ms, 1 325 s, 1 352 s, 1 359 s, 1 365 s, 1 376 s, 1 457 m, 1 717 s, 1 745 s, 1 764 s, 2 860 ms, 2 918 s.

Mass spectrum (m/e, relative intensity %, probably ionic species): 260/0.4 $(M)^{+\cdot}$, 135/86 $(C_{10}H_{15})^{+\cdot}$, 134/100 $(C_{10}H_{14})^{+\cdot}$, 133/31, 109/41 $(C_2F_3CO)^{+\cdot}$, 105/10, 94/39 $(C_7H_{10})^{+\cdot}$, 93/39 $(C_7H_9)^{+\cdot}$, 92/29, 81/22 $(C_2F_3)^{+\cdot}$, 79/24 $(C_6H_7)^{+\cdot}$, 78/18 $(CF_2CO)^{+\cdot}$, 77/26 $(C_6H_5)^{+\cdot}$, 67/23 $(C_5H_6)^{+\cdot}$, 56/19 $(C_4H_6)^{+\cdot}$.

For $C_{13}H_{15}F_3O_2$ (260.3) calculated/found: 60.0/60.2 %C, 5.8/6.0 %H, 22.0/21.7 %F.

^{19}F NMR spectrum:



F_A: dd -86.5, $^2J_{AB}$ 24, $^3J_{AX}$ 115

F_B: dd -96.8, $^3J_{BX}$ 35

F_X: dd -182.2

ACKNOWLEDGEMENTS

The spectral measurements were carried out in the Laboratories of NMR spectroscopy (Dr. P. Trška, Head), of mass spectrometry (Dr. V. Kubelka, Head), and of absorption spectroscopy (Dr. A. Muck, Head); the elemental analyses were performed in the Laboratory of organic analysis (Dr. L. Helešic, Head), all of the Institute of Chemical Technology, Prague.

We thank them all for their cooperation.

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