ELSEVIER

Journal of Fluorine Chemistry 90 (1998) 23–28

JOURNAL OF FLUORINE CHEMISTRY

A difluoro-substituted oxyallyl intermediate in [4+3] cycloadditions with cyclopentadiene and furan

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Received 5 August 1997; accepted 23 October 1997

Abstract

1-Bromo-1,3-difluoropropan-2-one (**2**) reacts with cyclopentadiene, furan and 2,5-dimethylfuran in 2,2,2-trifluoroethanol/sodium 2,2,2-trifluoroethoxide to form 2,4-difluorobicyclo[3.2.1]oct-6-en-3-one (**7b**) and the 8-oxa analogues (**7a**, **7c**). The *endo* orientation of the fluoro substituents at C-2 and C-4 indicates a concerted [4+3] cycloaddition of a W-configurated difluoro-oxyallyl intermediate (**5**) via a compact transition state.

Keywords: Oxyallyl intermediates; [4+3] Cycloaddition; Fluoro ketones; Bromination; Bicyclo[3.2.1]oct-6-en-3-ones; 2,2,2-Trifluoroethanol; Sodium 2,2,2-trifluoroethoxide

1. Introduction

Several α-chloro- and bromo ketones react in methanol or preferably 2,2,2-trifluoroethanol (TFE) in the presence of the corresponding alkoxide base, or triethylamine by an enolization–ionization mechanism. Dipolar species, called oxyallyls, have been postulated as reactive intermediates. They can be trapped with furan and some other 1,3-dienes, undergoing a [4+3] cycloaddition. The partition between this and other competing reaction pathways depends strongly upon the substitution pattern of the α-halogeno ketones [1–8].

Trichloro-, tetrachloro- and pentachloroacetone(s) have also been shown to give [4+3] cyclocoupling products with cyclopentadiene or furan(s) in TFE, 2,2,3,3-tetrafluoropropan-1-ol or lithium perchlorate/diethyl ether [1–3,9–11]. These additional chloro substituents in α- or α′-positions may stabilize the resulting oxyallyl intermediate by means of their donor character (+M effect). Furthermore, additional halogen substituents are known to exert an influence on the rate and the regiochemistry (α vs. α′-deprotonation) of the enolization step of the α-halogeno ketones [12–14]. The reductive generation of bromo-substituted oxyallyls from tetrabromoacetone may also be ascribed to a stabilizing donor effect of the bromo substituents [15–20] (for a solvolytic generation of oxyallyls from 1,3-dibromo-1-phthalimidopropan-2-one see Ref. [21]).

Among the halogens, fluorine as a substituent should exert the strongest donor effect, and thus would be expected to promote the ionization of the enolate, formed from a fluorinated α-halogeno ketone, for instance **2**→**1** (Scheme 1). However, the donor effect may be counterbalanced by the very strong σ-inductive effect (-*I*-effect) of the electron attracting fluoro substituent. On the other hand, ab initio calculations have pointed out that oxyallyls have a strong diradical character [22,23]. Therefore, the effects of fluoro substituents cannot be predicted reliably by this conventional reasoning.

A recent calculation for *Z,Z*-1,3-difluorooxyallyl (**5**) led to the conclusion that there is little difference in stability of the difluorinated (**5**) and the unsubstituted oxyallyl. However, the barrier of the disrotatory electrocyclic ring opening of *cis*-2,3-difluorocyclopropanone (**6**) was calculated to be about half as large as that of the parent cyclopropanone, and the cyclic valence isomer was found to be destabilized by the two fluoro substituents [24]. These computations prompt us to disclose our first studies with two fluoro-substituted α-halogenoacetones.

Following a procedure developed by Bergmann and Cohen [25], a mixture of 1-chloro-3-fluoropropan-2-ol and 1,3-difluoropropan-2-ol was obtained by reaction of epichlorohydrin with KHF_2. These alcohols were separated by rectification and oxidized to furnish 1-chloro-3-fluoroacetone and 1,3-difluoroacetone, respectively.

The latter ketone was made to react with one equivalent of molecular bromine in dichloromethane at room temperature.

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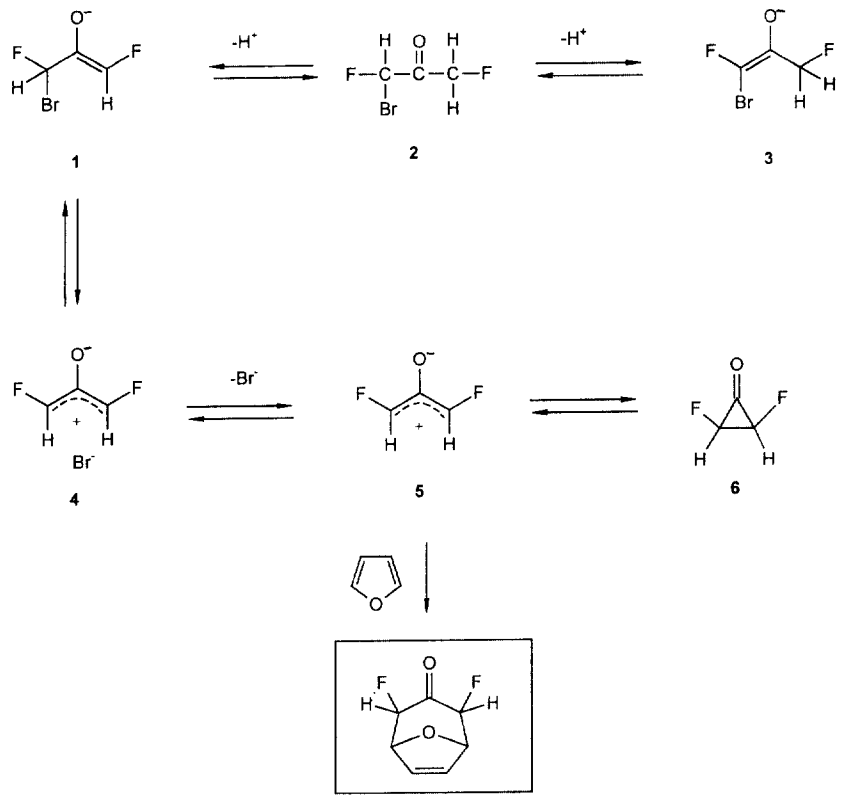
PII S0022-1139(98)00122-5



Scheme 1.

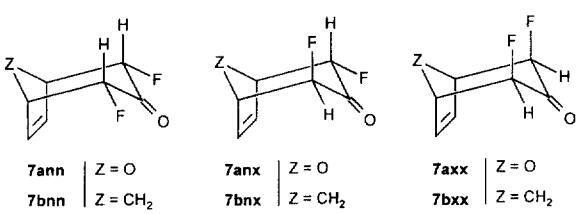
Monitoring by GC showed that the bromination was very sluggish; after four days, the peak of the educt had minimized. However, towards the end of the reaction time (approximately three days), a further peak at higher retention time arose in the GC trace, which was due to a dibromination product. The main component of the resulting mixture proved to be the expected 1-bromo-1,3-difluoroacetone (**2**). The product mixture was subjected to fractional distillation to furnish analytically pure **2** in 54% yield. A higher boiling fraction consisted of an inseparable mixture of two dibrominated difluoroacetones $C_3H_2Br_2F_2O$, presumably the *rac* and *meso* diastereomers of 1,3-dibromo-1,3-difluoropropan-2-one, as suggested by EI-MS and NMR spectra of the impure substance.

Our attempts to synthesize the corresponding 1-chloro-1,3-difluoroacetone by reacting 1,3-difluoroacetone with sulfuryl chloride were unsuccessful, yielding a complex inseparable product mixture.

The reaction of 1-chloro-3-fluoropropan-2-one with furan or 2,5-dimethylfuran in trifluoroethanol/sodium 2,2,2-trifluoroethoxide (TFE/NaTFE) [1–3] led to dark oils that proved to be complex mixtures (GC, TLC). We were not able to identify distinct components. Analyses by GC/MS gave no indication of fluoro-substituted oxabicyclic [4+3] cyclocoupling products.

On the other hand, 1-bromo-1,3-difluoropropan-2-one (**2**), under the same conditions, reacted with furan, 2,5-dimethylfuran, and cyclopentadiene, to give the expected 2,4-difluorobicyclo[3.2.1]oct-6-en-3-ones **7a–c**. However, yields were mediocre (19-38%). Of the three possible *endo/exo* diastereomers (***7nn***, ***7nx***, ***7xx***) we obtained in all cases exclusively the *endo, endo* (with respect to the fluoro substituents), by means of chromatography.

The NMR spectra reflect the mirror symmetry of the molecules consequently excluding the asymmetric *endo–exo* isomers.



In the proton noise-decoupled ^{13}C-NMR spectrum of the furan adduct **7a**, two of the four carbon resonances appear as doublets due to carbon/fluorine couplings. The coupling constants $J_{CF} = 204$ Hz and 23.3 Hz lead to the assignment C-2/C-4 (δ 90.87) and C-1/C-5 (δ 79.25), respectively. Com-

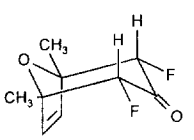
pared with the unsubstituted 8-oxabicyclo[3.2.1]oct-6-en-3-one ($\delta = 205.0$) [11], the weak carbonyl resonance of **7a** at δ 195.6 is shifted to higher field strength, but the effect of fluorine is smaller than that of chlorine in the analogous chloro bicycles [11]. The same trend is observed comparing **7b** and **7c** with their dehalogenated parent ketones.

In the ^{1}H-NMR (C_6D_6 solvent) of **7a**, both the bridge-head protons and the protons at C-2/C-4 appear as doublets of doublets (coupling with the neighboring hydrogen and fluorine atoms). In $CDCl_3$, the bridge-head protons of **7a** generate a not well resolved multiplet. The vicinal proton/proton coupling constant $J_{12} = J_{45} = 5.2$ Hz is characteristic for the coupling of the *exo*-protons (2-H, 4-H) with the bridge-head hydrogen atoms, thus giving a firm proof for the *endo* orientation of both fluorine atoms at C-2 and C-4.

As expected, the NMR spectra of the cyclopentadiene adduct **7b** are more complicated. Inter alia, the carbon atom of the methylene bridge, is coupled with the fluorine atoms, giving a triplet ($^3J_{CF} = 9.7$ Hz). From the ^{1}H-NMR spectrum, a vicinal proton/proton coupling constant $^3J_{12} = {}^3J_{45} = 3.8$ Hz can be derived. In the corresponding *endo/endo* dichloro bicycle a vicinal coupling constant $^3J_{12} = {}^3J_{45} = 3.3$ Hz has been observed [11].

In the cycloadduct of **5** with 2,5-dimethylfuran (**7c**) the methyl groups at the bridge-heads prevent a determination of the configuration at C-2/C-4 by means of ^{1}H-NMR coupling constants. However, the nearly identical values of the carbonyl chemical shifts in the ^{13}C-NMR for **7a** ($\delta = 195.6$) and **7c** ($\delta = 195.9$) indicate the same configuration, i.e., *endo,endo* at C-2 and C-4.

In general, apart from the complications by the H/F-couplings, the spectral data of the difluoro ketones **7a–c** are closely related to the spectra of the corresponding *endo-endo*-dichloro bicycles [11].



7cnn

2. Conclusion

2,4-Difluorobicyclo[3.2.1]oct-6-en-3-one (**7b**) and the two 8-oxa analogues (**7a**, **7c**) have been isolated from the reaction of 1-bromo-1,3-difluoroacetone (**2**) with cyclopentadiene, furan, and 2,5-dimethylfuran in TFE/NaTFE. These products are rationalized to arise from a [4+3] cycloaddition of an oxyallyl intermediate formed from **2** via an enolization–ionization mechanism. This is in contrast to the behaviour of the unsubstituted oxyallyl or cyclopropanone, which was never observed to undergo [4+3] cycloadditions with 1,3-dienes. This leads us to the conclusion that fluoro substituents stabilize the oxyallyl intermediate. The *endo* configuration of the isolated bicyclic compounds are in agreement with a concerted [$_\pi 4_s + _\pi 2_s$] cycloaddition of the W-configurated, i.e., (*Z,Z*)-1,3-difluorooxyallyl (**5**) via a compact transition state [26–29].

It should be considered that the yield of halogeno-substituted [4+3] cycloadducts generated from 1,1,3-trichloro-2-propanone is generally higher than with the fluoro analogue **2** [11]. Is the stabilizing effect of two chloro substituents stronger than that of two fluoro groups? Since the cycloaddition is the last step of a complex process (Scheme 1), this argument is attractive, but not conclusive.

As a matter of course, in Scheme 1 a mechanism is suggested in a simplified form. It is likely that TFE is associated to the negatively charged oxygen atoms of the enolates and the oxyallyls via hydrogen bonds (for recent calculations on solvent effects with oxyallyls, see Ref. [23]). Furthermore, our experiments cannot exclude that the bicycles are formed directly from the ion pair **4** by nucleophilic attack of the electron rich 1,3-diene π-system.

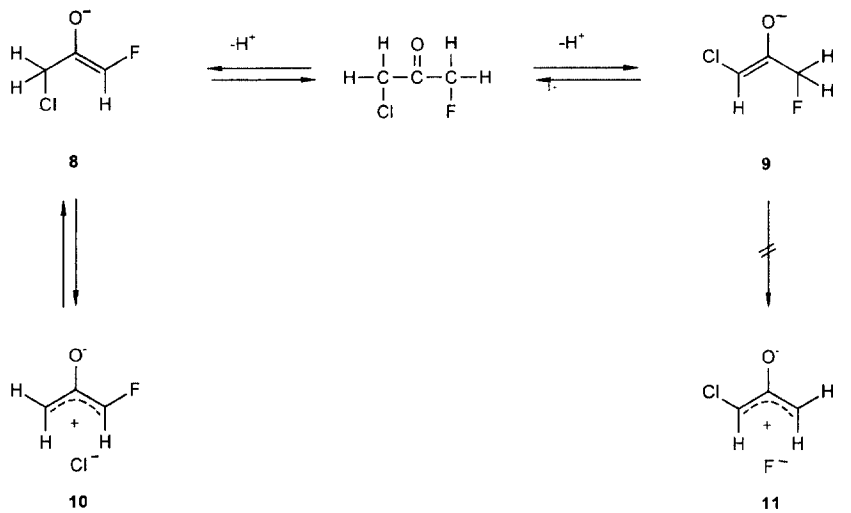
The failure to obtain a bicyclic product from 1-chloro-3-fluoropropan-2-one, i.e., to trap the monofluorooxyallyl (**10**), parallels the behaviour of 1,3-dichloropropan-2-one [11] and may have two reasons: (1) Enolization leads to the 'wrong' enolate (**9**), ultimately forming self-condensation products [12–14]; (2) The ionization of the 'right' enolate (**8**) is too slow, i.e., only one fluoro substituent is not sufficient to assist the ionization and to stabilize the oxyallyl (**10**) Scheme 2.

3. Experimental

Proton and carbon-13 NMR spectra were recorded as solutions in $CDCl_3$ on a Bruker CXP 300 instrument. Chemical shifts are reported in ppm from tetramethylsilane as internal standard. The multiplicities of the signals are described as either s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). A Perkin-Elmer 457 instrument was used to record the infrared spectra. Mass spectra were obtained by electron impact ionization (EI) at 70 eV on a Varian MAT 711 instrument with data system SS 100. High-resolution measurements were obtained by the peakmatch method using perfluorokerosine (PFK) as reference.

2,2,2-Trifluoroethanol (TFE) is commercially available in high purity (GC > 99%, Fluka, *puriss.*, or ABCR, Karlsruhe) and was used directly, without further purification. Solutions of sodium 2,2,2-trifluoroethoxide (NaTFE) were prepared by adding small (!) cut pieces of sodium to TFE at room temperature. (Caution: If the sodium is added too rapidly, i.e., the local amount of sodium is too large, overheating can occur; in one of some dozens of preparations, the reaction mixture decomposed with charring and ignition, even under inert gas!)

Dichloromethane was refluxed over powdered calcium hydride and distilled. Commercial furan (Merck) was shaken



Scheme 2.

with an aqueous potassium hydroxide (5%) solution. The organic layer was separated from the aqueous phase and dried over KOH pellets. It was distilled prior to use. 2,5-Dimethylfuran was prepared from hexan-2,5-dione according to the procedure of Scott and Naples [30].

Chromatographic purifications were carried out using Merck Kieselgel 60, particle size 63–200 μm.

3.1. 1-Bromo-1,3-difluoropropan-2-one (2)

Bromine (7.99 g, 50.0 mmol) was added dropwise to a stirred solution of 1,3-difluoropropan-2-one (4.70 g, 50.0 mmol) in dry dichloromethane (10 ml), with continuous stirring. The red colour of the bromine faded very slowly. After 4 days, the mixture became slightly orange red. In order to remove HBr, a saturated solution of sodium hydrogen carbonate was added dropwise and with caution, until the evolution of carbon dioxide ceased. The mixture was extracted with diethyl ether (3×30 ml) and the combined extracts dried with magnesium sulfate. After evaporation of the solvents, the remaining liquid was fractionated using a 20-cm Vigreux column at reduced pressure. The main fraction distilled at 65–68°C/35–40 Torr yielding **2** (4.71 g, 54%) as a colourless liquid.

^{13}C-NMR (75.5 MHz, $CDCl_3$, off-resonance): $\delta = 81.17$ (d, $^1J_{CF} = 185$ Hz, C-3), 84.70 (d, $^1J_{CF} = 264$ Hz, C-1), 193.84 (dd?, appearance of a t, $^2J_{CF} = 21$ Hz, C-2).

^{1}H-NMR (300 MHz, $CDCl_3$) $\delta = 5.21$ (ddd, $^2J_{HF} = 46.8$ Hz, $^2J_{3a3b} = 16.9$ Hz, $^4J_{HF} = 2.0$ Hz, 1H, 3-H_a), 5.39 (dd, $^2J_{HF} = 46.2$ Hz, $^2J_{3a3b} = 16.8$ Hz, 1H, 3-H_b), 6.84 (dd, $^2J_{HF} = 50.6$ Hz, $^4J_{HF} = 2.0$ Hz, 1H, 1-H).

IR (film): 3500, 3015, 2950, 1760, 1435, 1390, 1360, 1315, 1218, 1196, 1180, 1147, 1070, 1030, 1010, 880, 845, 778, 715, 689, 628, 598.

$C_3H_3BrF_2O$ (172.96) calc. C 20.83, H 1.75, Br 46.20; found C 20.81, H 1.90, Br 46.17%.

3.2. endo-2, endo-4-Difluoro-8-oxabicyclo[3.2.1]oct-6-en-3-one (7ann)

Under a nitrogen atmosphere, a mixture of 1-bromo-1,3-difluoropropane-2-one (**2**) (1.73 g, 10.0 mmol) and 10 ml freshly distilled furan was cooled to −18°C. To the stirred solution NaTFE in TFE ($c = 2.0$ mol/l, 5 ml, 10 mmol) was added dropwise in about 5 min. After 10 min, no starting material **2** could be detected by gas chromatography; a white precipitate (sodium chloride) was formed. Stirring was continued (50 min) at room temperature; the color of the mixture changed to yellowish. Water (10 ml) was added and the mixture was extracted with diethyl ether (6×20 ml). The combined ether layers were dried with magnesium sulfate and concentrated in a rotary evaporator. The dark brown oily residue (1.72 g) was purified by column chromatography (20 g silica, petroleum ether/ethyl acetate (24:1) and ***7ann*** (0.31 g, 19%) was isolated as a white solid. Recrystallization from dichloromethane/petroleum ether furnished colorless needles with m.p. 108°C.

^{13}C-NMR (75.5 MHz, $CDCl_3$): $\delta = 79.25$ (d, $^2J_{CF} = 23.3$ Hz, C-1 and C-5), 90.87 (d, $^1J_{CF} = 204$ Hz, C-2 and C-4), 133.02 (s, C-6 and C-7), 195.58 (low intensity, C-3).

^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 5.07$ (dd, $^2J_{HF} = 47.5$ Hz, $^3J_{12} = {}^3J_{45} = 5.2$ Hz, 2H, exo-2-H and exo-4-H), 5.27 (m, 1-H and 5-H), 6.46 (s, 2H, 6-H and 7-H).

^{1}H-NMR (300 MHz, C_6D_6): $\delta = 4.23$ (dd, $^2J_{HF} = 47.9$ Hz, $^3J_{12} = {}^3J_{45} = 5.2$ Hz, 2H, exo-2-H and exo-4-H), 4.36 (dd, $^3J_{12} = {}^3J_{45} = 5.2$ Hz, $J = 0.7$ Hz, 2H, 1-H and 5-H), 5.71 (s, 2H, 6-H and 7-H).

IR (KBr): 3120, 3000, 2970, 1740, 1705, 1590, 1390, 1340, 1300, 1285, 1265, 1240, 1210, 1110, 1085, 1070, 1000, 975, 945, 935, 890, 870, 815, 750, 670, 625, 525, 450, 370.

EI-MS (70 eV): m/z (%) = 140 (16) [M - HF], 112 (100) [M - (HF + CO)], 99 (34), 84 (16), 83 (12), 72 (32), 71 (18), 68 (12), 51 (34), 46 (11), 39 (22).

HRMS Calc. for $C_7H_5FO_2$ [M-HF] 140.0274, found 140.0272 $C_7H_6F_2O_2$ (160.12) calc. C 52.51, H 3.78. found C 52.32, H 3.71%.

3.3. endo-2, endo-4-Difluorobicyclo[3.2.1]oct-6-en-3-one (7bnn)

Cyclopentadiene (8 ml, ca. 97 mmol) was prepared by cracking distillation of commercial dicyclopentadiene, and immediately mixed with **2** (1.73 g, 10.0 mmol) under nitrogen. With magnetic stirring, a solution of NaTFE in TFE (c=2.0 mol/l, 5 ml, 10 mmol) was added dropwise at −18°C. After 15 min, no starting material **2** could be detected by gas chromatography; a white precipitate (sodium chloride) was formed. The mixture darkened after stirring at room temperature for 60 min. Water (20 ml) was added, and the mixture was extracted with dichloromethane (6×25 ml). The combined organic layers were dried with magnesium sulfate and concentrated under reduced pressure. The dark oily residue (1.45 g) was purified by column chromatography (20 g silica, petroleum ether/ethyl acetate (20:1). The first fractions contained mainly dicyclopentadiene and a small amount of ***7bnn***. The residue from the evaporated middle fractions was recrystallized from petroleum ether/ethyl acetate (20:1) affording 0.51 g (32%) ***7bnn*** as a white solid with m.p. 145–146°C.

^{13}C-NMR (75.5 MHz, $CDCl_3$): δ=34.72 (t, $^3J_{CF}$=9.7 Hz, C-8), 44.95 (d, $^2J_{CF}$=18.5 Hz, C-1 and C-5), 94.46 (d, $^1J_{CF}$=197.8 Hz, C-2 and C-4), 134.70 (s, C-6 and C-7), 198.61 (t, $^2J_{CF}$=14.3 Hz, C-3).

^{1}H-NMR (300 MHz, $CDCl_3$): δ=1.84 (d, $^2J_{8n8x}$=12.8 Hz, 1H, endo-8-H), 2.34 (mc, 1H, exo-8-H), 3.26 (mc, 2H, 1-H and 5-H), 5.01 (dd, $^2J_{HF}$=48.2 Hz, $^3J_{12}$=$^3J_{45}$=3.8 Hz, 2H, exo-2-H and exo-4-H), 6.22 (finely split s, 2H, 6-H and 7-H).

IR (KBr): 3080, 2990, 2980, 2930, 1740, 1460, 1360, 1300, 1290, 1270, 1240, 1160, 1100, 1085, 1020, 1005, 990, 955, 950, 940, 900, 870, 805, 755, 670, 635, 610, 480, 445.

EI-MS (70 eV): m/z (%) = 158 (52, M), 138 (33) [M-HF], 118 (7), 115 (17), 110 (12), 109 (26), 98 (29), 97 (100), 96 (8), 95 (13), 93 (6), 91 (9), 84 (6), 83 (9), 79 (23), 78 (6), 77 (14), 70 (5), 66 (15), 65 (5), 59 (7), 57 (9), 51 (16), 50 (5), 39 (16), 33 (5).

HRMS calc. for $C_8H_8F_2O$: 158.0543, found 158.0545 $C_8H_8F_2O$ (158.15) Calc. C 60.76, H 5.10; found C 60.05, H 5.07%

3.4. endo-2, endo-4-Difluoro-1,5-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (7cnn)

2,5-Dimethylfuran (1.92 g, 20.0 mmol), **2** (1.73 g, 10.0 mmol) and NaTFE solution (c=2.0 mol/l, 5 ml) were stirred for 30 min at 0°C, and 1 h at room temperature. The reaction mixture was worked up as described for the preceding compound ***7bnn***. After chromatography with petroleum ether/ethyl acetate (10:1), ***7cnn*** was obtained as a white solid with m.p. 109–110°C. Yield 0.71 g (38%).

^{13}C-NMR (75.5 MHz, $CDCl_3$): δ=19.91 (s, 1-CH_3 and 5-CH_3), 86.36 (d, $^2J_{CF}$=21.2 Hz, C-1 and C-5), 94.60 (d, $^1J_{CF}$=205.9 Hz, C-2 and C-4), 135.55 (s, C-6 and C-7), 195.86 (low intensity, C-3).

^{1}H-NMR (300 MHz, $CDCl_3$): δ=1.61 (finely split s, 6H, 1-CH_3 and 5-CH_3), 4.72 (d, $^2J_{HF}$=49.0 Hz, 2H, exo-2-H and exo-4-H), 6.14 (s, 2H, 6-H and 7-H).

EI-MS (70 eV): m/z (%) = 188 (48, M), 168 (14) [M-HF], 140 (46) [M-(HF+CO)], 128 (20), 127 (23), 126 (16), 125 (11), 113 (71), 109 (14), 97 (14), 96 (31), 95 (40), 85 (25), 65 (11), 59 (10), 43 (100).

HRMS calc. for $C_9H_{10}F_2O_2$: 188.0649, found 188.0647 $C_9H_{10}F_2O_2$ (188.17) Calc. C 57.45 H 5.36, found C 54.96, H 5.39%

Acknowledgements

We thank Messrs. J. Rebell and Dr. W. Rozdzinski for recording the NMR and mass spectra, respectively.

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