Journal of Fluorine Chemistry
Elsevier Sequoia S.A., Lausanne — Printed in Switzerland

Short Communication

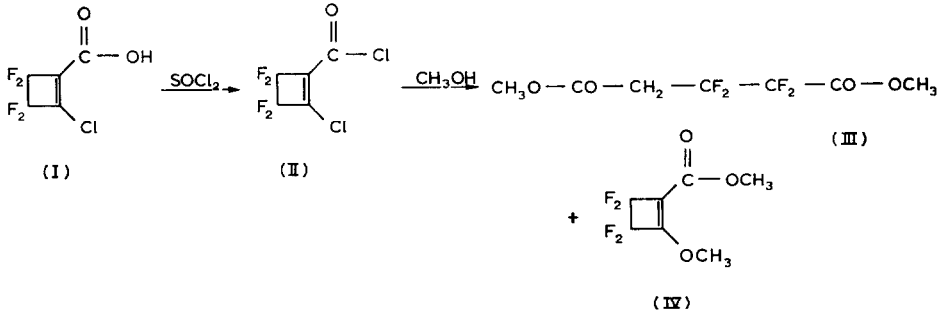
Methanolysis of 2-chloro-1-chloroformyltetrafluorocyclobutene

R. L. SOULEN* AND J. D. PARK

Department of Chemistry, University of Colorado, Boulder, Colorado 80302 (U.S.A.)

(Received September 16, 1972)

In our continuing investigation of the chemistry of perfluorocycloalkene carboxylic acids[1], we have prepared 2-chloro-1-chloroformyltetrafluorocyclobutene (II) and attempted the preparation of the corresponding methyl ester. Excess methanol and the acid chloride (I) were mixed at room temperature causing the solution to reflux spontaneously for several minutes. After refluxing overnight, the solution was fractionally distilled and the high boiling fractions separated by gas chromatography into two major products, (III) and (IV).



(I) (II) (III) (IV)

Compound (III) has been identified as methyl 2,2,3,3-tetrafluoroglutarate and compound (IV) as methyl 2-methoxy-1-tetrafluorocyclobutene carboxylate based on the following data.

The infrared spectrum of (III) gave two close bands in the carbonyl region (5.62 and 5.70 μ) as well as other bands which supported the general structure. The ^{1}H NMR spectrum gave two singlets of equal area at 3.68 δ and 3.42 δ corresponding to $\underline{CH_3}$–O–CO–CF_2 and $\underline{CH_3}$–O–CO–CH_2 absorptions, respectively, and a triplet of triplets at 2.90 δ ($J = 18$ Hz and ~ 1 Hz) corresponding to the –CF_2–$\underline{CH_2}$–$COOCH_3$ absorption. Using Shoolery's[2] constants, the calculated value for the methylene proton absorption is 2.92 δ. These H–F coupling constants and the chemical shifts are within reported values[2] for similar structures.

* Department of Chemistry, Southwestern University, Georgetown, Texas 78626 (U.S.A.).

The ^{19}F NMR spectrum of (III) gave a singlet at 120.3 ppm and a triplet (J = 18 Hz) at 112.9 ppm of equal area. The signal at 120.3 ppm is similar to values reported previously for a CF_2 group adjacent to an ester carbonyl[3].

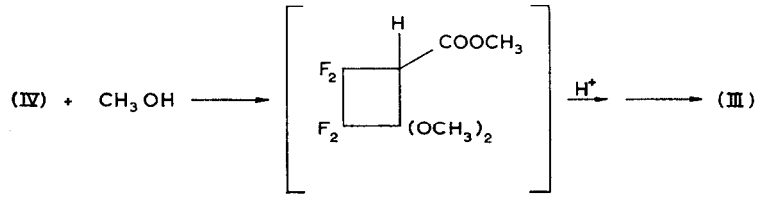
The mass spectrum fragmentation pattern of (III) was consistent with the assigned structure but did not exclude the possibility of the isomeric structure, CH_3O–CO–CF_2–CH_2–CF_2–CO–OCH_3. However, the previously discussed ^1H and ^{19}F spectra would not support this arrangement.

The infrared spectrum of (IV) gave a carbonyl absorption at 5.78 μ and a broadened olefinic band at 5.98 μ typical of conjugated methyl vinyl ethers[4]. The ^1H NMR spectrum consisted of two singlets of equal area at 3.70 and 4.25 δ. Previously reported values for 1-methoxy-pentafluorocyclobutene[5] permit assignment of the signal at 3.70 δ to the $\underline{CH_3}$–O–C= group and the 4.25 δ signal to the $\underline{CH_3}$–O–CO– group. The ^{19}F spectrum gave equal area multiplets at 113.9 and 120.6 ppm characteristic of an AA'BB' system.

The mass spectrum fragmentation pattern of (IV) was consistent with the assigned structure. Loss of CH_3, CH_3O and $COOCH_3$ from the molecular ion gave rise to the most prominent ions; however, in contrast to (III), the loss of HF was not observed.

The appearance of compound (IV) among the methanolysis products of the acid chloride (II) was not wholly unexpected. The first step of this reaction undoubtedly involves formation of the simple ester and release of HCl. Substitution of the vinylic chlorine atom could occur by either nucleophilic attack by methanol and subsequent loss of chloride ion or by addition of methanol to the double bond and subsequent loss of HCl. In view of the acidic character of the methanol solution, the latter pathway seems more realistic.

The formation of (III) by ring scission of tetrafluorocyclobutene was quite surprising. To our knowledge, only one other example of a similar hydrolytic opening appears in the literature. Barney and Cairns[6] have reported that 1-cyano-2,2,3,3-tetrafluorocyclobutane reacted with aqueous base or acid to give only 2,2-difluoroglutaric acid. An intermediate formation of 2,2-difluorocyclobutanone-4-carboxylic acid was suggested. A similar cyclobutanone intermediate can be envisioned from (IV) by the addition of methanol across the double bond and subsequent acid-catalyzed decomposition of the dimethyl ketal.



Acid-catalyzed ring opening of the cyclobutanone leads directly to (III).

Experimental

2-Chlorotetrafluorocyclobutene-1-carboxylic acid (I)

The compound was prepared as described by Park *et al.*[1].

2-Chlorotetrafluorocyclobutene-1-carboxylic acid chloride (II) (nc)

Thionyl chloride (25 ml) and 9.68 g (0.047 mole) of the crude acid (I) were heated to reflux for 2.5 days then fractionally distilled, collecting 8.24 g (78%) between 104–109° at 628 mmHg. A center cut b.p. 109°/628 mmHg gave strong IR absorption at 5.68 (C=O), 6.20 (C=C) and 7.5–8.5 μ (C–F) but no bands above 5.5 μ. (Found: C, 26.62; H, <0.2; Cl, 31.63%. $C_5F_4Cl_2O$ requires C, 26.93; Cl, 31.80%.)

Reaction of (II) with anhydrous methanol

Reagent methanol (9 ml) was added rapidly to 5.7 g (0.025 mole) of (II) causing the mixture to reflux spontaneously for several minutes. Reflux was continued overnight then the liquid was quickly fractionated and a crude higher boiling fraction collected (4.6 g, b.p. 115–130°/30 mmHg). The crude product was separated by VPC using a 4.8 m $\times$ 5 mm column containing 20 wt. % SF–1265 on Chromosorb W at 200° (50 ml He min^{-1}). Two major products (90% of the total) were collected, (III) and (IV), both new compounds.

Compound (III) appeared from the column after 7.5 min; 1.15 g (20%); IR (neat) 3.32 and 3.38 (C–H), 5.62 and 5.70 (C=O), 7.5–8.2 (C–F), 8.5–10.0 μ (C–O); ^{1}H NMR, 3.68 δ (singlet), 3.42 δ (singlet), 2.90 δ (triplet, $J = 18$ Hz) in a 3:3:2 ratio; ^{19}F NMR, 120.3 ppm (singlet), 112.9 ppm (triplet, $J = 18$ Hz) in a 1:1 ratio; mass spectrum, 232 (1.30%), 201 (23%), 181 (60%), 153 (29%), 123 (46%), 59 (100%). (Found: C, 36.13; H, 3.54; F, 33.54%. $C_7H_8F_4O_4$ requires C, 36.22; H, 3.47; F, 33.74%.)

Compound (IV) appeared from the column after 9 min; 2.68 g (49%); IR (neat) 3.32 and 3.38 (C–H), 5.78 (C=O), 5.98 (C=C), 7.5–8.0 (C–F), 9.0–10.0 μ (C–O); ^{1}H NMR, 3.70 δ (singlet), 4.25 δ (singlet) in a 1:1 ratio; ^{19}F NMR, 113.9 ppm (multiplet), 120.6 ppm (multiplet); mass spectrum, 214 (10%), 199 (51%), 195 (14%), 185 (24%), 183 (47%), 155 (27%), 59 (46%), 15 (100%). (Found: C, 38.88; H, 2.73; F, 35.19%. $C_7H_6F_4O_3$ requires C, 39.26; H, 2.83; F, 35.49%.)

We wish to thank the 3M Company and AFOSR Chemical Division for their support of this work.

REFERENCES

1 J. D. Park, C. D. Bertino and B. T. Nakatá, *J. Org. Chem., 34* (1969) 1490.
2 L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon Press, New York, 2nd ed., 1969.

3 Y. K. KIM, *J. Org. Chem., 32* (1967) 3672.
4 R. L. SOULEN, D. B. CLIFFORD, F. F. CRIM AND J. A. JOHNSTON, *J. Org. Chem., 36* (1971) 3386.
5 A. B. CLAYTON, R. STEPHENS, D. R. SAYERS, J. ROYLANCE AND J. C. TATLOW, *J. Chem. Soc.,* (1965) 7358.
6 A. L. BARNEY AND T. L. CAIRNS, *J. Amer. Chem. Soc., 72* (1950) 3193.