Journal of Fluorine Chemistry, 16 (1980) 285–292

Received: May 28, 1980

REACTION OF CRYSTALLINE FLUORO OLEFINS WITH BROMINE VAPOR.

3. SOLID-STATE STEREOSPECIFICITY FOR (E) AND (Z)-2-(4'-CARBOXYPHENYL)-1-CHLORO-1-FLUOROETHENE. [1]

DOUGLAS G. NAAE

Department of Chemistry, University of Kentucky
Lexington, Kentucky, 40506 (U.S.A.)

SUMMARY

The gas-solid addition reaction between gaseous bromine and solid (E) and (Z)-4-$HO_2CC_6H_4CH{=}CFCl$ has been examined. Reaction under ionic conditions leads to predominant anti-addition of bromine (80% anti for the E isomer; 90% for Z). Addition under radical conditions is slightly stereoselective with a small excess (54:46 for E; 56:44 for Z) of the S,R diastereomer of 4-$HO_2CC_6H_4CHBrCFClBr$ being formed. It is concluded that this olefin system has greater freedom of molecular motion in the solid than 4-$HO_2CC_6H_4CF{=}CFX$ ($X{=}Cl$, CF_3).

INTRODUCTION

The stereochemistry of the gas-solid addition of halogens to solid olefins is dependent upon the structure of the intermediate involved in the reaction. Solid α,β unsaturated acids, amides and ketones yield trans-dibromo adducts, as an intermediate bromonium ion is involved and anti addition of bromine occurs [2-6]. In contrast, chlorine adds in a syn manner to solid trans-stilbene via an open cation [7]. Previously we had reported the gas-solid reactions between bromine and (E) and (Z)-4-$HO_2CC_6H_4CF{=}CFCl$, (1), and (E) and (Z)-4-$HO_2CC_6H_4CF{=}CFCF_3$, (2), [1]. For (1) predominant anti-addition occurs under ionic conditions while attempts to achieve radical addition in the solid-state were only partly successful as the ionic reaction competed favorably with the radical reaction. Predominate syn-addition of bromine was found for the ionic and radical reactions of Z-(2).

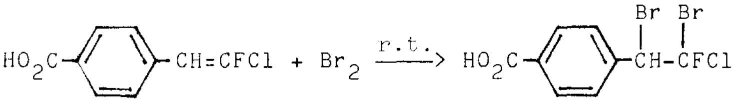
This report extends this work to (E) and (Z)-4-$HO_2CC_6H_4CH{=}CFCl$, (3). In solution this olefin exhibits anti addition of bromine under ionic conditions [8] and almost non-stereoselective addition under radical conditions. It represents an opportunity to determine if an ionic reaction leading to anti-addition can be suppressed to allow syn-addition via a radical reaction in the solid-state.

RESULTS AND DISCUSSION

The results of the gas-solid reactions are given in Table I and several observations can be made. The ionic reactions (Exp. Nos. 1,2,4,5) occur more readily at higher bromine concentrations. While this could be explained by a melt

Table I

Gas-Solid Bromination Reactions[a]



(solid) (gas) (R,R) and (S,R) diastereomers

Exp. No.	Isomer	Reaction Conditions[b]	Olefin: Bromine Ratio	Yield, %[c]	Ratio (R,R): (S,R)[c]	Anti: Syn
1	E	Dark, 5d	9:20	<5	--	--
2	E	Dark, 13d	4:55	100	20:80	4.0:1
3	E	hν, 3d	9:20	50	46:54	--
4	Z	Dark, 5d	14:21	<5	--	--
5	Z	Dark, 5d	15:55	100	90:10	9.0:1
6	Z	hν, 3d	15:20	25	44:56	--
7	Z	hν, 2d	15:55	95	76:24	3.2:1
8	Z	hν, 4d[d]	15:55	100	87:13	6.7:1

a. Procedures are given in the experimental section.
b. For hν reactions, illumination was by a 60-watt incandescent lamp 25 cm from the reaction vessel, except as noted.
c. Reaction yield and diastereomeric product ratios were determined by ^{1}H nmr, ± 3%. Isomerization of the starting olefin was not observed in any of the reactions.
d. The incandescent lamp was 60 cm from the reaction vessel.

formation which facilitates the reaction, none could be detected by microscopic examination of solid (3) during the reaction. A more plausible explanation is that the ionic addition of bromine to (3) is predominantly 2nd order in bromine [8-12]. Therefore, a high concentration of bromine is required for the ionic reaction.

The amount of *anti*-addition to E-(3) is comparable to that found for Z-(1) (these olefins have the same relative configurations, the Cl and $HO_2CC_6H_4$ groups are *trans*). However, the amount of *anti*-addition to Z-(3) is significantly greater than that to E-(1) (9.0:1 versus 2.6:1) [1]. In acetic acid the two olefin systems exhibit comparable amounts of *anti*-addition [8]. The increase in the amount of *anti*-addition for Z-(3) can be attributed to greater molecular motion in the solid (relative to E-(1)) which permits easier formation of a bromonium ion and subsequent molecular movement. This premise of increased molecular motion in solid (3) is also supported by the radical reactions.

The gas-solid radical addition reactions of (3) (Nos. 3,6,7,8) exhibit the following trends. The olefins are reactive at either high or low bromine concentration, with the reaction at low concentration being indicative of a radical reaction involving bromine atoms. Under conditions of exclusive radical reaction (Nos. 3,6) the addition is slightly stereoselective and the diastereomer ratio is very close to the solution value of 42:58 (R,R:S,R). No preference for *syn* addition is observed; this is in contrast with solid (2) where substantial *syn*-addition was observed for the radical reactions (1:2.4-anti:syn for Z-(2) and 1:1.6 for E-(2)) [1].

The influence of the α-H in (3) versus the α-F in (1) and (2) is difficult to assess. There appears to be an effect as the diastereomer ratio for (3) is 42:58 (R,R:S,R) for a radical addition while the ratio for (1) is 25:75 for solution reactions [1,8]. The decrease in the ratio could be due to a change in the hybridization of the α-carbon in the intermediate radical or to a difference in steric size of H versus F; although these atoms are often considered to be sterically similar [13]. Whatever the nature of the difference between (1) and (3) it is evident that (3) has more freedom of motion in the solid as it reaches the equilibrium diastereomer ratio values easier than either (1) or (2) do.

Table I also shows that at high bromine concentration (Exp. No. 7) there is competition between the radical and ionic additions. This is reflected in an increase in the amount of *anti*-addition. A decrease in the intensity of the light source (No. 8) leads to a further increase in the amount of *anti*-addition as the ionic reaction becomes even more dominant. These trends were also observed in the gas-solid reactions of (1) [1].

EXPERIMENTAL

Melting points were determined on a hot stage and are uncorrected. ^{1}H NMR spectra were obtained on a Varian HFT-80 Fourier Transform spectrometer. Mass spectral analysis was performed on a Perkin-Elmer Hitachi RMU-7 double-focusing mass spectrometer. A Wild M-7 trinocular polarizing microscope was used for microscopic observation of the gas-solid reactions.

Preparation of (E) and (Z)-4-$HO_2CC_6H_4CH{=}CFCl$ (nc)

4-$BrC_6H_4CH{=}CFCl$ was prepared and the isomers separated by preparative GLC on 20% Apeizon-L [8,14]. The separated isomers were then converted to the acid via a Grignard reagent by the previously described procedure [15]. Each isomer was purified by fractional sublimation and recrystallized from toluene. E-4-$HO_2CC_6H_4CH{=}CFCl$: m.p. = 208-212°C; mass spectrometry, M^+ at 202, 200 m/e; ^1H nmr, δ (vinyl H) = 6.24 ppm (d), J(H,F) = 31.4 Hz, $\delta(C_6H_4)$ = 7.61 ppm (AB quartet); Z-4-$HO_2CC_6H_4CH{=}CFCl$: m.p. = 157-160°C; mass spectrometry, M^+ at 202, 200 m/e; ^1H nmr, δ(vinyl H) = 6.77 ppm (d), J(H,F) = 13.1 Hz, $\delta(C_6H_4)$ = 7.65 ppm (AB quartet). The ^1H nmr spectra correspond to that reported for (E) and (Z)-4-$XC_6H_4CH{=}CFCl$ (X = CH_3, Br) [8].

Gas-Solid Reactions with Bromine

The previously described procedure was used [1]. Thus, ca. 15 mg. of the powdered olefin was placed in one side of a deeply creased 20-mL flask. The flask was flushed with nitrogen and the appropriate amount of liquid bromine (see Table I) was added to the other side of the flask. The flask was stoppered and either placed in a light-tight box or illuminated by a 60 watt tungsten lamp. After the reaction time was complete the flask was opened and the excess bromine was allowed to escape. The sample was dissolved in acetone-d_6, and the ^1H nmr spectrum was recorded to determine the diastereomeric product ratio and the per-cent yield. Other product peaks were not observed in the ^1H nmr.

The structural assignment of the product, 4-$HO_2CC_6H_4CHBrCFClBr$, was accomplished by mass spectrometry, M^+ at 364, 362, 360, 358 m/e, and ^1H nmr: (R,R) δ (H) = 6.25 ppm (d), J(H,F) = 12.4 Hz, δ (C_6H_4) = 7.3-7.9 ppm (m); (S,R) δ (H) = 6.18 ppm (d), J(H,F) = 17.4 Hz, δ (C_6H_4) = 7.3-7.9 ppm (m). These nmr parameters correspond to the values previously reported for 4-$XC_6H_4CHBrCFClBr$ (X = CH_3, Br) [8].

Solution Bromination of 4-$BrC_6H_4CH{=}CFCl$.

The previously described procedure for radical bromination in CCl_4 was used. It has been found for olefins with electron-withdrawing substituents on the aromatic ring that the diastereomeric product ratio is independent of substituent, solvent, or reactant concentration [8]. Approximately 0.60 mmol of the olefin was weighed into an nmr tube, followed by 0.25 mL of CCl_4 and 25 µL (0.50 mmol) of neat bromine. The reaction mixture was irradiated by a 60 watt tungsten lamp. After five minutes, the ^1H nmr spectrum was recorded. Isomerization of the starting olefin did not occur and a 42:58 (R,R:S,R) product ratio of 4-$BrC_6H_4CHBrCFClBr$ was observed.

REFERENCES

1 Previous paper in series: D.G. Naae, J. Org. Chem., 44 (1979) 336.

2 E. Hadjoudis, E. Kariv, and G.M.J. Schmidt, J. Chem. Soc., (1972) 1056.

3 E. Hadjoudis and G.M.J. Schmidt, J. Chem. Soc., (1972) 1060.

4 E. Hadjoudis, Isr. J. Chem., 11 (1973) 63.

5 E. Hadjoudis, Isr. J. Chem., 12 (1974) 981.

6 E. Hadjoudis in J. Wood, O. Lindqvist, C. Helgesson, and N.-G. Vannerberg (Editors), Reactivity of Solids, Plenum Press, New York, 1977, p. 493.

7 R.S. Miller, D.Y. Curtin, and I.C. Paul, J. Am. Chem. Soc., 94 (1972) 5117.

8 D.G. Naae, J. Org. Chem., 45 (1980) 1394.

9 K. Yates, R.S. McDonald and S.A. Shapiro, J. Org. Chem., 38 (1973) 2460.

10 K. Yates and W.V. Wright, Can. J. Chem., 45 (1967) 167.

11 H.P. Rothbaum, I. Ting, and P.W. Robertson, J. Chem. Soc., (1948) 980.

12 J.H. Rolston and K. Yates, J. Am. Chem. Soc., 91 (1969) 1483.

13 R.D. Chambers, Fluorine in Organic Chemistry, Wiley-Interscience, New York, 1973, Chapter 1.

14 M.J. Van Hamme and D.J. Burton, J. Fluorine Chem., 10 (1977) 131.

15 D.G. Naae, J. Org. Chem., 42 (1977) 1780.