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FLUORINE CONTROL OF STEREOSPECIFITY AND REGIOSELECTIVITY IN PHOTOCYCLOADDITION REACTIONS. CYCLOADDITION REACTIONS OF 1,1–DIPHENYL–2–FLUOROETHYLENE

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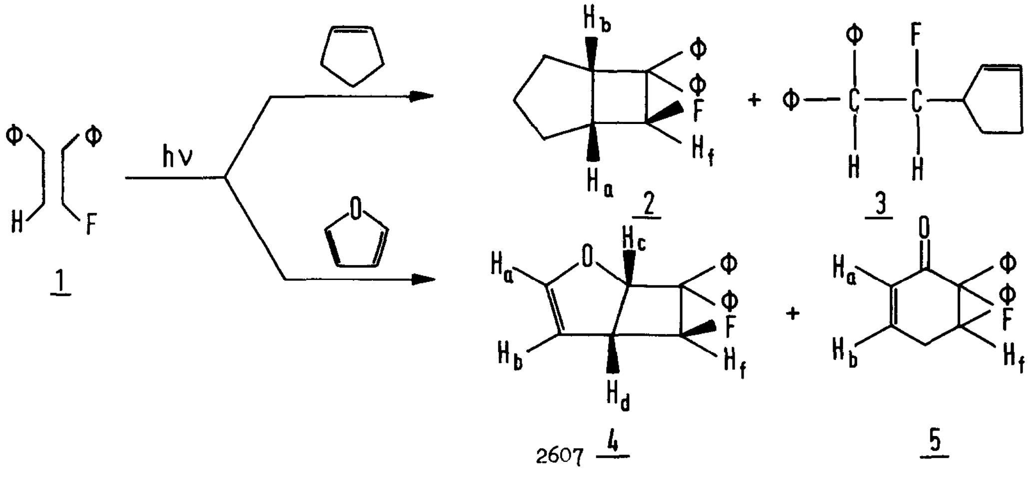
The photocycloaddition reactions of 1,1–diphenylethylene have been studied in the presence of various alkenes[1]. Cantrell has shown that the excited triplet state of 1,1–diphenylethylene gave 2 + 2 cycloadducts[1b] in the presence of certain olefins. The fluorine atom as a substituent has been used several times as a marker in photochemical transformations[2]. We now report results of studies on the stereochemistry of the cycloaddition of excited 1,1–diphenyl–2–fluoroethylene (1) to cyclopentene and furane.

Irradiation of 1 mmol of 1 in 18 ml of cyclopentene for 15 hours at λ = 253.7 nm at room temperature resulted in a crude reaction mixture, which showed in its ^{19}F nmr spectrum two signals in the ratio 1 : 2.7 (2 : 3). Products were isolated by preparative tlc and the structures of the products were determined on the basis of their nmr, mass and ir spectra. The major product formed (3, 3–(1–fluoro–2,2–diphenylethyl)–cyclopentene–1, liquid product, 31 %), showed in its ^{19}F nmr spectrum a ddd signal at δ = – 184.8 ppm and in proton resonance the following signals: δH : 3.24 ppm (1 H,d, $^{3}J_{FH}$ 19.5 Hz), 4.7 ppm (1 H,d, $^{2}J_{FH}$ 57 Hz), 3.05 ppm (1 H,m), 5.6 ppm (2 H,m), 1.75 ppm (4 H,m) and 7.2 ppm (10 H,m). Mass spectrum: calcd. for $C_{19}H_{19}F$ m/e 266.1470, found m/e 266.1468, m/e: 266 (M^{+}, 15 %), 246 (31), 244 (15), 217 (20), 199 (67), 198 (100), 197 (20), 179 (20), 178 (20), 167 (23), 165 (33), 115 (26), 91 (28), 67 (51). The minor product formed (2, anti–6–fluoro–7,7–diphenylbicyclo [3,2,0] heptane, 12 %) showed in its ^{19}F nmr one doublet of doublet signal at – 232.5 ppm ($^{2}J_{FH_f}$ = 60 Hz, $^{3}J_{FH_a}$ = 18 Hz), and in its proton spectrum the following signals: δH_f = 5.03 ppm (dd, $^{3}J_{H_fH_a}$ = 4.5 Hz), $\delta H_a,H_b$ = 3.02 ppm (m), $\delta C\underline{H}_2$ = 1.6 ppm (6 H,m) and δPh = 7.1 ppm (10 H,m). Mass spectrum: calcd. for $C_{19}H_{19}F$ m/e 266.1470, found m/e 266.1470, m/e: 266 (M^{+}, 6%), 199 (50), 198 (87), 197 (17), 179 (28), 178 (41), 165 (46), 68 (100), 67 (34). The 2+2 cycloaddition reaction proceeded stereospecifically so that only anti-isomer was formed and the stereochemistry was assigned on the known variation of $^{3}J_{FH_a}$ and $^{3}J_{H_fH_a}$ with dihedral angle[3].

The above mentioned stereospecifity stimulated us to study the reaction of 1,1–diphenyl–2–fluoroethylene with furane, which resulted in two products (4 and 5) under the above–mentioned conditions.



The structures of the products were determined on the basis of their nmr, mass and ir spectral data. 2+2 photocycloaddition occurred stereospecifically and regiospecifically, thus forming anti-6,6-diphenyl-7-fluoro-4-oxobicyclo [3,2,0] heptene-2 (4, mp 72−74°C, 23%) which showed in its ^{19}F nmr spectrum one signal at −187.5 ppm (dm, $^2J_{FH_f}$ = 57 Hz, $^3J_{FH_d}$ = 12 Hz, $^4J_{FH_c}$ = 6 Hz and $^4J_{FH_b}$ = 4.5 Hz), and in its proton spectrum the following signals: δH_a = 6.3 ppm(m), δH_f = 5.6 ppm (dd, $^3J_{FH_d}$ 4 Hz), δH_c = 5.3 ppm (m), δH_b = 4.95 ppm (m) and δH_d 4.4 ppm (m). Mass spectrum: m/e: 266 (M^+,1%), 199 (15), 198 (100), 197 (46), 196 (36), 185 (12), 165 (28), 98 (16), 85 (10). Elemental analysis: calcd. for $C_{18}H_{15}OF$: % C 81.18, % H 5.68, found % C 80.86, % H 5.36. The second product formed (5, 20% of liquid product) showed in its ^{19}F nmr spectrum a doublet of triplet signal at −187.13 ppm with $^2J_{FH_f}$ = 57 Hz and $^3J_{FH}$ = 10 Hz, and in its proton spectrum the following signals: δH_a = 6.15 ppm (m), δH_f = 5.45 ppm (dd), δH_b = 4.84 ppm (m), δCH_2 4.25 ppm(m) and δPh 7.2 ppm (10 H,m). Mass spectrum: calcd. for $C_{18}H_{14}O$ (M^+− HF) m/e 246.1044, found m/e 246.1044, m/e: 266 (M^+,2%), 246 (9), 205 (27), 199 (16), 198 (100), 197 (37), 196 (27), 165 (25), 69 (36). In its ir spectrum it showed a signal at ν = 1720 cm^{-1}, characteristic of a conjugated carbonyl group. On the basis of the spectroscopic data, we established that 2,2-diphenyl-3-fluorocyclohexene-5-on-1 (5) was formed. Product 5 was not formed by photorearrangement of product 4. Its formation could be ascribed to 2+4 cycloaddition, followed by rearrangement. The stereochemistry of 2+2 photoproduct 4 was assigned on the known variation of $^3J_{H_fH_d}$ with dihedral angle and long range coupling constant $^4J_{FH_c}$. The addition of 1 to cyclopentene or furane was quenched by piperylene. Photocycloaddition reactions of cis- or trans-fluorostilbene with cyclopentene or furane did not occur, which could be explained by a different type of stabilization of excited state. At the present time we have no reasonable explanation for stereospecific 2+2 photoadditions.

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