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Reaction of nitroalkanes with polyfluoroaromatic compounds

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ABSTRACT

Nitromethane and nitroethane in the presence of DBU attack preferentially the para position of pentafluorobenzonitrile and methyl pentafluorobenzoate to give the addition products in good yield. The resulting nitro compounds can be converted to tetrafluorotoluene or ethyl benzene derivatives by tri-*n*-butyltin hydride. $TiCl_3$ solution neatly transforms the nitroethyl compounds into corresponding ketones. With a base, the nitro compounds can be used to extend chain length using Michael acceptors like ethyl acrylate and acrylonitrile.

1. Introduction

Polyfluoroaromatic compounds by virtue of the presence of large number of fluorine atoms undergo nucleophilic aromatic substitution (S_NAr) [1] in contrast to normal aromatic compounds which give rise to substitution products arising out of electrophilic substitution. This unique property of polyfluoroaromatic systems has been studied thoroughly with variety of nucleophiles having oxygen [2], nitrogen [3] or sulfur [4] atoms and many such reactions have been exploited as a part of synthetic strategy to make substitution products with the above nucleophiles. However, the number of such reactions with carbon nucleophiles [5] is very few though the formation of carbon–carbon bond by this procedure should be synthetically more rewarding.

S_NAr reactions follow addition–elimination mechanism by the intermediacy of Meisenheimer complex which has been proposed in quite a few systems [6]. To form such a complex, a negative charge stabilizing group like cyano, carbomethoxy or nitro is required. Except for special reasons attributed to stabilization of intermediates by any of these groups by incoming nucleophiles in the ortho position, most of the reactions follow a pathway wherein the predominant product is para directed. Many theories have been put forward to explain this para selectivity [6,7].

Nitroalkanes are versatile reagents in that, by forming the carbanion α- to the nitro group, strong nucleophiles are produced which can initiate S_NAr reactions. Moreover, the products formed from these reactions can be transformed into other useful compounds on one hand and on the other the nitrogroup can be utilized as a handle for effecting new nucleophilic reactions [8]. This paper describes in brief the reaction of nitromethane and nitroethane with pentafluorobenzonitrile (PFBN) and methyl pentafluorobenzoate (MPFB) to determine the regiospecificity of such reactions. To the best our knowledge such reactions are reported for the first time (see below). Some typical further transformations are also described.

2. Results and discussion

Nitromethane in the presence of a strong organic base such as DBU reacts with PFBN to provide a product mixture, the analysis of which showed >97% para selectivity in ether (Scheme 1). Upon isolation and recrystallization, the product could be purified further. That the product obtained is para substituted is ascertained by all spectral data, the most important being two symmetrical signals of equal intensity in the ^{19}F NMR spectrum. Similar results were obtained for nitromethane addition to MPFB and nitroethane to both substrates (Scheme 1). These results are in stark contrast to the results reported recently by Sandford group, wherein monoaryl addition product could not be isolated [9]. Perhaps in the pyridine derivative benzyl proton being more acidic deprotonation occurs readily forcing into react with another pyridine nucleus.

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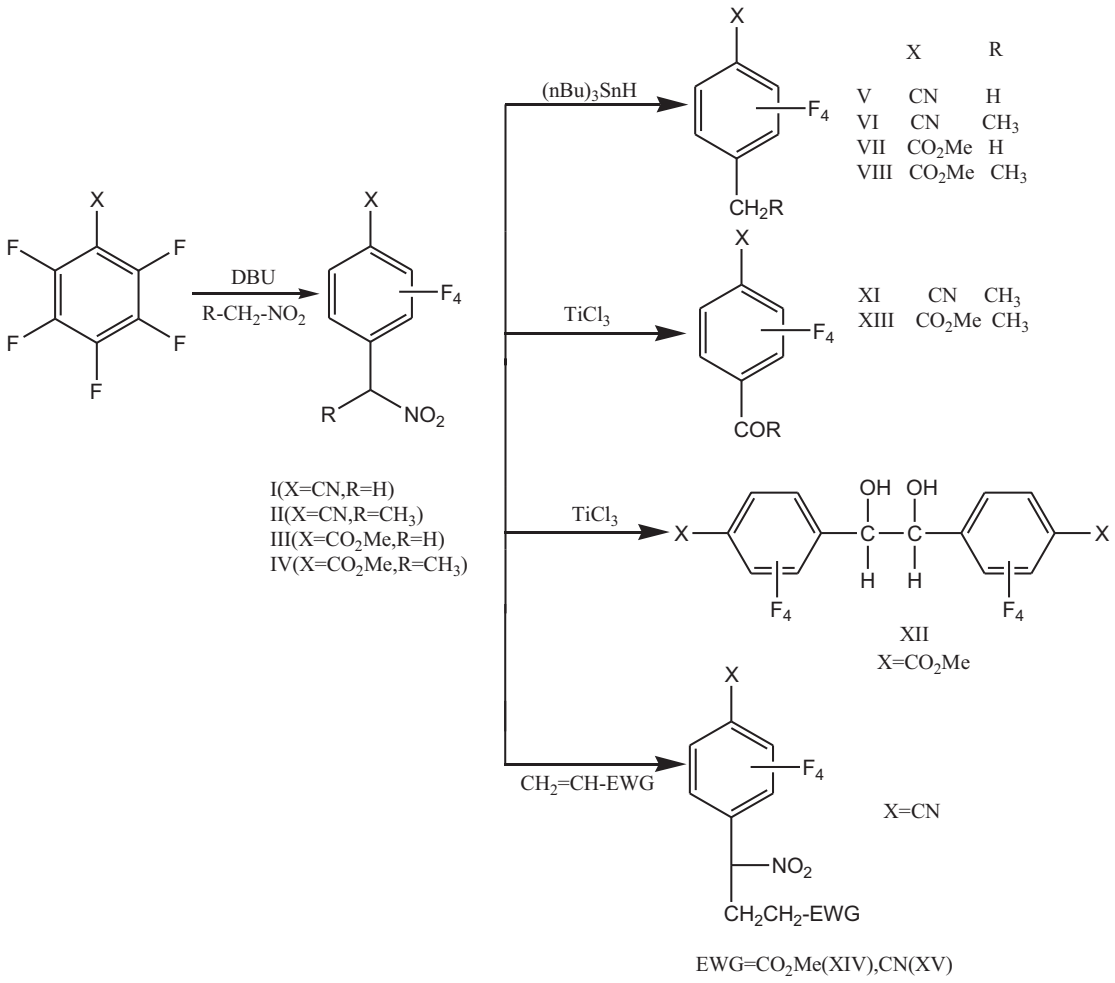


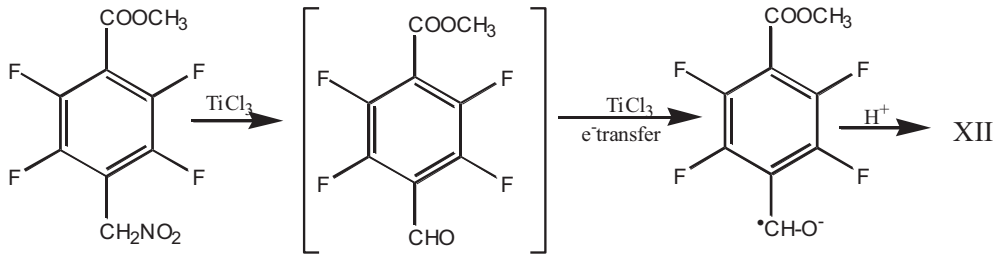
Scheme 1.

Since, many nucleophilic reactions are affected by the solvent polarity, we investigated the selectivity and extent of reaction in three solvents namely acetonitrile, THF and benzene. The results with PFBN and nitromethane showed that the selectivity to para position is not influenced by the polarity of the solvent (range 2.5–4.5% ortho).

α-Aryl nitroalkanes are versatile intermediates [8a]. Reduction with tri-*n*-butyltin hydride afforded the corresponding methyl or ethyl aryl compounds (V–VIII) in very good yield. In general, this free radical mediated reaction is facile only with secondary and tertiary nitro compounds. In this case, the presence of highly electronegative aryl ring perhaps facilitates the removal of even primary nitrogroup easily. It is worth noting that V is an important intermediate for the synthesis of tefluthrin, an insecticide. This procedure is a clean laboratory preparative method for this intermediate as other methods of preparation of this compound involve several steps [10].

Next we attempted Nef reaction [8]. In basic medium, $KMnO_4$/$MnSO_4$/KOH did convert I to the corresponding aldehyde (IX) albeit in low yield (<11%). Other reagents in basic medium did not improve the results [11,12]. Most likely, the arylnitro compounds are susceptible to further addition of hydroxyl group in the ortho position in the basic medium resulting in low yield.

Nef reactions can be done in acid medium also using $TiCl_3$ as a reagent. This gave some surprising results with primary nitro compound III. Instead of the expected aldehyde, III underwent further reduction to provide a mixture of products including a pinacol. We envisage that the mechanism of formation of pinacol is through the intermediate aldehyde. Being adjacent to a highly electronegative group this aldehyde accepts one more electron to



Scheme 2.

give a radical anion, which upon dimerization and subsequent protonation provides the pinacol [13] (Scheme 2). In the case of secondary nitro compounds, the ketones were obtained in excellent yield.

With DBU as a base, I adds on to both acrylonitrile and ethyl acrylate smoothly to provide the corresponding Michael addition products as shown in Scheme 1.

All the new products obtained were confirmed by spectral data.

3. Conclusions

Nitromethane and nitroethane under basic condition add to pentafluorobenzonitrile and methyl pentafluorobenzoate predominantly to the para position. The nitrocompounds so formed can be transformed into variety of products by conversion of the nitrogroup. They also serve as versatile intermediates for extension of chain length through Michael reaction.

4. Experimental details

^{1}H, ^{19}F and ^{13}C NMR were recorded in Bruker A VIII 500 MHz spectrometer. For ^{1}H and ^{13}C NMR TMS and ^{19}F $CFCl_3$ were used as internal standards. Analysis in GC–MS and GC were performed in Agilent instruments 5973 and 6890, respectively. IR was recorded in Perkin Elmer spectrum one FTIR spectrometer.

All solvents and chemicals were purified by standard procedures. PFBN is a commercial product of SRF with 99.7% purity (GC). MPFB was prepared from pentafluorobenzoic acid and methanol and distilled prior to use (purity 99.5%).

4.1. Reaction of pentafluorobenzonitrile (PFBN) with nitromethane (I)

In a three-necked flask having a mechanical stirrer, inlet for nitrogen and an addition funnel was taken DBU (7.61 g, 0.05 mol) and 50 ml of dry ether. This solution was cooled to 0 °C and nitromethane (3.05 g, 0.05 mol) in 25 ml of ether was added dropwise. Yellow color developed. After stirring for ten more minutes, PFBN (4.83 g, 0.025 mol) in 25 ml of ether was added dropwise (30 min). About the middle of the reaction, precipitate appeared but the mixture could be stirred continuously. After maintaining at 0 °C for half an hour more, dil. HCl was added till the mixture became acidic. The ether layer was separated. The aqueous layer was extracted twice with ether and combined with the ether layer. The solution was washed with $NaHCO_3$, dried over Na_2SO_4, filtered and the solvent evaporated on a water bath kept at 45 °C, then vacuum was applied to the residue to remove excess of nitromethane. The semisolid mass obtained was recrystallized from ethanol, m.p. 65–65.5 °C. Yield: 4.56 g (78%). IR (KBr) 2250, 1563, 1500, 1371 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.70 (t, J = 1.5 Hz, –CH_2–). ^{19}F NMR (470.4 MHz, $CDCl_3$) δ −130.5 (m, 2 and 6), −137.1 (m, 3 and 5) [refer to the numbering in Scheme 1]. EI-MS (70 eV) 188 [$(M-NO_2)^+$ (100)]. CI-MS 235 [$(M+H)^+$ (100)]. HR-MS 235.0132 [calculated for $C_8H_3N_2O_2F_4$ = 235.0131].

4.2. Reaction of PFBN with nitroethane (II)

Use of nitroethane instead of nitromethane in the above procedure gave a liquid product which was purified by chromatography as it was contaminated with small amount of corresponding ketone (silica gel, 50% benzene–hexane). The product obtained was distilled in a bulb to bulb distillation assembly, b.p. 120–125 °C/1 mm. Yield: 4.21g (68%). IR (Neat) 2249, 1563, 1497, 1360 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.64 (1H, q, J_{H-H} = 7.2 Hz), 1.82 (3H, d, J_{H-H} = 7.2 Hz). ^{19}F NMR (470.4 MHz, $CDCl_3$) δ −130.7 (dd, J_{F-F} = 17.9 and 10.3 Hz, 2 and 6), −138.0 (dd, J_{F-F} = 17.9 and 9.9 Hz, 3 and 5). EI-MS (70 eV) 202 [$(M-NO_2)^+$ (100)]. CI-MS 249 [$(M+H)^+$ (100)], 202 [$(M-NO_2)^+$ (68)].

Satisfactory HRMS could not be obtained for this compound as it degrades under the ESI condition but on reduction with TBTH and reaction with $TiCl_3$ it provides VI and XI, respectively, both of which have satisfactory HRMS data.

4.3. Reaction of methyl pentafluorobenzoate (MPFB) with nitromethane (III)

To a solution of ether (50 ml) and DBU (7.61 g, 0.05 ml) at −10 °C was added dropwise nitromethane (3.05 g, 0.05 mol) in 25 ml ether. After half an hour stirring, MPFB (5.90 g, 0.025 mol) dissolved in 25 ml of ether was added dropwise. Stirring was continued for 1 h more at the same temperature. After this period, dil. HCl was added, ether layer was separated, aqueous layer was extracted with ether and combined ether solution was washed with sodium bicarbonate solution till neutral, dried and solvent evaporated. Applying vacuum to the residue, provided a viscous liquid which upon refrigeration solidified. This was crystallized from cold methanol at 4 °C, m.p. 30–31 °C. Yield: 5 g (75%). IR (Neat) 1744, 1570, 1491, 1373 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.01 (3H, s, –OCH_3), 5.66 (2H, t, J_{HF} = 1.5 Hz, –CH_2–). ^{19}F NMR (470.4 MHz, $CDCl_3$) δ −138.3 (dd, J_{F-F} = 24.9 and 15.5 Hz, 2 and 6), −139.9 (dd, 25.0 and 16.0 Hz, 3 and 5). EI-MS (70 eV) 236 [$(M-OCH_3)^+$ (14)], 221 [$(M-NO_2)^+$ (100)]. CI-MS 268 [$(M+H)^+$ (42)], 221 [$(M-NO_2)^+$ (100)]. HR-MS 290.0053 [calculated for $C_9H_5NO_4F_4Na$ = 290.0052].

4.4. Reaction MPFB with nitroethane (IV)

Use of nitroethane in the place of nitromethane in the above procedure provided a solid which was recrystallized from cold methanol, m.p. 59–60 °C. Yield: 5.69 g (81%). IR (KBr): 1737, 1563, 1489, 1366 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87 (1H, q, J_{H-H} = 7.5 Hz, –CH–NO_2), 4.02 (3H, s, –OCH_3), 2.04 (3H, d, J_{H-H} = 7.5 Hz, CH_3–CH=). ^{19}F NMR (470.4 MHz, $CDCl_3$) δ −137.9 (dd, J_{F-F} = 21 and 13 Hz, 2 and 6), −140.3 (dd, J_{F-F} = 21 and 13 Hz, 3 and 5). EI-MS (70 eV) 250 [$(M-OCH_3)^+$ (6)], 235 [$(M-NO_2)^+$ (100)]. CI-MS 282 [$(M+H)^+$ (47)], 235 [$(M-NO_2)^+$ (100)]. HR-MS 304.0205 [calculated for $C_{10}H_7NO_4F_4Na$ = 304.0209].

4.5. Reaction of nitro compounds with tri-n-butyltin hydride

In a two necked flask having a magnetic stirrer, condenser and a guard tube was taken I–IV (1 mmol). Tri-*n*-butyltin hydride (340 mg, 1.17 mmol), catalytic amount of azobisisobutyronitrile (32 mg) and benzene (5 ml) were charged and the mixture was heated to reflux for two hrs. The contents were concentrated on a rotary evaporator and the residue chromatographed on silica gel to provide the corresponding alkyl compounds in good yield. GC purity ranged from 98% to 99%.

V colorless liquid, b.p. 100–5 °C/20 mmHg. Yield: 113 mg (60%). IR (Neat) 2249, 1496, 1302 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.40 (t, J_{H-F} = 2.0 Hz, CH_3). ^{19}F NMR (470.4 MHz, $CDCl_3$) δ −134.5 (m, 2 and 6), −140.2 (m, 3 and 5). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.94 (ddt, J = 241, 16.5, 3.5 Hz, C-2 and C-6), 144.97 (m, C-3 and C-5), 123.906 (t, J = 18.8 Hz, C-4), 107.64 (t, J = 3.5 Hz, CN), 91.69 (t, J = 17 Hz, C-1), 8.43 (s, CH_3). EI-MS (70 eV) 189 [M^+ (100)], 188 [$(M-H)^+$ (91)]. HR-MS 190.0274 [calculated for $C_8H_4NF_4$ = 190.0280].

VI colorless liquid, b.p. 100–5 °C/10 mmHg. Yield: 132 mg (65%). IR (Neat) 2242, 1493, 1249, 1172 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.86 (2H, m, CH_2), 1.29 (3H, t, J = 7.5 Hz, CH_3). ^{19}F NMR (470.4 MHz, $CDCl_3$) δ −133.38 (dd, J_{F-F} = 17.4 and 9.4 Hz, 2 and 6), −141.83 (dd, J_{F-F} = 17.4 and 9.4 Hz, 3 and 5). EI-MS (70 eV) 203 [M^+

(43)], 188 [$(M-CH_3)^+$ (100)]. HR-MS 204.0439 [calculated for $C_9H_6NF_4$ = 204.0436].

VII colorless liquid, b.p. 105–107/1 mmHg. Yield: 137 mg (62%). IR (Neat) 1744, 1489, 1313 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 3.98 (3H, s, $-OCH_3$), 2.33 (3H, t, J_{H-F} = 2 Hz). ^{19}F NMR (470.4 MHz, $CDCl_3$) δ −140.8 (dd, J_{F-F} = 20.2 and 11.8 Hz, 2 and 6), −142.35 (dd, J_{F-F} = 20.2 and 11.8 Hz, 3 and 5). EI-MS (70 eV) 222 [M^+ (36)], 191 [$(M-OCH_3)^+$ (100)]. HR-MS 223.0375 [calculated for $C_9H_7O_2F_4$ = 223.0382].

VIII colorless liquid, b.p. 128–130 °C/1 mmHg. Yield: 160 mg (68%). IR (Neat) 1745, 1487, 1306 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 3.99 (3H, s, OCH_3), 2.81 (2H, m, $-CH_2CH_3$), 1.26 (3H, t, J = 7.5 Hz, $-CH_3$). ^{19}F NMR (470.4 MHz, $CDCl_3$) δ −140.5 (dd, J_{F-F} = 20 and 11.7 Hz, 2 and 6), −144.44 (dd, J_{F-F} = 20 and 11.7 Hz, 3 and 5). EI-MS (70 eV) 236 [M^+ (30)], 205 [$(M-OCH_3)^+$ (100)]. HR-MS 237.0541 [calculated for $C_{10}H_9O_2F_4$ = 237.0539].

4.6. Nef reaction of I with $KMnO_4/MnSO_4/KOH$ (IX)

To the nitro compound I (12 g, 0.05 mol) in methanol (200 ml) kept between 0 and 5 °C under nitrogen atmosphere, was added dropwise freshly made KOH solution (3.14 g, 0.056 mol). After a few minutes stirring at 0 °C, a freshly made aq. $KMnO_4$ (5.90 g, 0.037 mol) and $MgSO_4{\cdot}7H_2O$ (9.28 g, 0.038 mol) were added with vigorous stirring. After stirring for an additional hour at 0 °C, the mixture was filtered through a layer of celite and the filtrate extracted with benzene (3× 50 ml). It was treated with brine and the organic layer was separated and dried and distilled under vacuum to remove the solvent. The residue slowly crystallized but had a very low shelf stability and could not be characterized fully. Yield: 1.14 g (11%). ^1H NMR (500 MHz, $CDCl_3$) δ 10.34 (s). EI-MS (70 eV) 203 [M^+ (98)], 202 [$(M-H)^+$ (100)].

4.7. Nef reaction of III with $TiCl_3$ (XII)

To a solution of 12% $TiCl_3$ (12 ml) and ammonium acetate (3.0 g) was added III (267 mg, 1 mmol) in THF (5 ml). The solution was stirred for 3 h under nitrogen atmosphere. A violet colored slurry was obtained. This was extracted with ether (5× 10 ml) and washed with sodium bicarbonate solution till neutral. The solution was dried, solvent evaporated and the residue was analyzed by GC–MS. It showed a number of products. On keeping at RT, a solid separated, which was recrystallized from methanol–benzene, m.p. 217–218 °C. Yield: 65 mg (27%). IR (Neat) 3507 (doublet), 1724, 1485, 1334, 1315 cm^{-1}. ^1H NMR (500 MHz, CD_3OD) δ 5.52 (1H, s, $\underline{CH}$–OH), 4.00 (3H, s, $-OCH_3$). ^1H NMR (500 MHz, CD_3CN) δ 5.44 (1H, dd, J = 4.0 and 2.0 Hz, $C\underline{H}$–OH), 4.21 (1H, bt, OH), 4.00 (3H, s, $-OCH_3$) CD_3CN (D_2O shake), δ 5.41 (1H, s, $-C\underline{H}-$), 3.95 (3H, s, $-OCH_3$). ^{13}C NMR (125 MHz, CD_3OD) δ 160 (s, $COOCH_3$), 145.4 (m, C-2 and 6), 144.4 (m, C-3 and 5), 124.1 (t, J = 15 Hz, C-4), 111.9 (t, J = 16.5, C-1), 67.0 (s, $-\underline{C}HOH$), 52.3 (s, OCH_3). ^{19}F NMR (470.4 MHz, $CDCl_3$) −142.86 (dd, J = 20 and 12 Hz (2,2′ and 6,6′)), −143.8 (bs, 3,3′ and 5,5′). ESI-MS 475 [$(M+H)^+$ (100)]. HR-MS 497.0247 [calculated for $C_{18}H_{10}O_6F_8Na$ = 497.0247].

4.8. Nef reaction of II and IV with $TiCl_3$ (XI and XIII)

To a solution of 12% $TiCl_3$ (12 ml) and ammonium acetate (3.0 g) was added II or IV (1 mmol) in THF (5 ml) under nitrogen atmosphere and the solution was stirred for 5 h at room temperature. A violet colored slurry appeared. This was extracted with ether (5× 10 ml) and washed with sodium bicarbonate solution till neutral. The solution was dried, solvent evaporated and the residue distilled through a bulb to bulb distillation assembly.

XI A colorless liquid, b.p. 105–110 °C/1 mmHg. Yield: 177 mg (82%). IR (Neat) 2250, 1720, 1488, 1313 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 2.66 (t, J_{H-F} = 1.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3 (s, CO), 147.3 (dddd, J_{C-F} = 264, 16.6, 4.4, 1.9 Hz, C-2 and C-6), 143.4 (m, the major coupling constant is 250 Hz, C-3 and C-5), 125.1 (t, J = 18.3 Hz, C-4), 106.8 (t, J = 3.6 Hz, CN), 96.3 (t, J = 17 Hz, C-1), 32.33 (d, J = 11.75 Hz, CH_3). ^{19}F NMR (470.0 MHz, $CDCl_3$) −130.21 (dd, J_{F-F} = 19.2 and 11.7 Hz, 2 and 6), −138.73 (dd, J_{F-F} = 19.2 and 11.7 Hz, 3 and 5). EI-MS (70 eV) 217 [M^+ (48)], 202 [$(M-CH_3)^+$ (100)], 174 [$M-COCH_3$ (36)]. CI-MS 218 [$(M+H)^+$ (100)]. HR-MS 240.0040 [calculated for $C_9H_3NOF_4Na$ = 240.0048].

XIII A colorless liquid, b.p. 128–130 °C/1 mmHg. Yield: 175 mg (70%). IR (Neat) 2962, 1747, 1715, 1479, 1319 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 4.03 (3H, s, $-OCH_3$), 2.66 (3H, t, J = 2 Hz, $COCH_3$). ^{19}F NMR (470.4 MHz, $CDCl_3$) δ −137.72 (dd, J = 21.6, 13.5 Hz, 2 and 6), −140.5 (dd, J = 21.6 and 13.5 Hz, 3 and 5). EI-MS (70 eV) 250 [M^+ (42)], 235 [$(M-CH_3)^+$ (100)]. CI-MS 251 [$(M+H)^+$ (100)].

Satisfactory HRMS data for the intact compound could not be obtained. Therefore 2,4-dinitrophenyl hyrazone of compound XIII was prepared by standard procedure; recrystallized from methanol, m.p. 120–121 °C. IR (KBr) 3302, 1748, 1620, 1596, 1506, 1474, 1338, 1314 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 11.39 (1H, s, NH), 9.18 (1H, d, J = 2.5 Hz, H_3'), 8.38 (1H, dd, J = 9.5 and 2.5 Hz, H_5'), 7.99 (1H, d, J = 9.5 Hz, H_6'), 4.02 (3H, s, $-OCH_3$), 2.47 (3H, s, $-CCH_3$). HR-MS 453.0434 [calculated for $C_{16}H_{10}N_4O_6F_4Na$ = 453.0434].

4.9. Reaction of I with ethylacrylate (XIV)

To a solution of I (234 mg, 1 mmol) in acetonitrile (5 ml) was added ethylacrylate (110 mg, 1.1 mmol) and DBU (167 mg, 1.1 mmol) and stirred for 3 h at room temperature under N_2 atmosphere. GC showed absence of starting material after this period. This brown solution was diluted with ether, washed with dil. HCl to remove the base and dried and purified by column chromatography.

XIV slight amber colored viscous liquid, homogenous on HPLC. Yield: 304 mg (91%). IR (Neat) 2987, 2250, 1732, 1566, 1497, 1370 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 6.02 (1H, t, J = 7.0 Hz, $-C\underline{H}-NO_2$), 4.17 (2H, q, J = 7 Hz, $-O-CH_2-$), 3.04 (1H, m, >CH–C$\underline{H}$H*–), 2.60 (1H, m, >CH–CH$\underline{H}$*), 2.47 (2H, m, $-\underline{CH_2}-COO$), 1.28 (3H, t, J = 7.0 Hz, $-CH_2\underline{CH_3}$). EI-MS (70 eV) 288 [$(M-NO_2)^+$ (30)], 260 [$(M-COOEt)^+$ (100)]. CI-MS 335 [$(M+H)^+$ (100)], 288 [$(M-NO_2)^+$ (68)]. HR-MS 357.0470 [calculated for $C_{13}H_{10}N_2O_4F_4Na$ = 357.0474].

4.10. Reaction of I with acrylonitrile (XV)

To a solution of I (234 mg, 1 mmol) in acetonitrile (5 ml) was added acrylonitrile (79 mg, 1.5 mmol) and DBU (167 mg, 1.1 mmol) and reaction performed as above. The product was isolated as an amber colored liquid after silica gel chromatography.

XV amber colored viscous liquid, homogenous on HPLC. Yield: 210 mg (73%). IR (Neat) 2962, 2251, 1566, 1498, 1362, 1302 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 5.91 (1H, t, J = 7 Hz, $-C\underline{H}-NO_2$), 3.09 (1H, m, >CH–C$\underline{H}$H*–), 2.68 (1H, m, >CH–CH$\underline{H}$*), 2.62 (1H, m, $-C\underline{H}$H*–CN), 2.50 (1H, m, $-CH\underline{H}$*–CN). EI-MS (70 eV) 241 [$(M-NO_2)^+$ (21)], 188 [(100)]. CI-MS 288 [$(M+H)^+$ (100)], 241 [$(M-NO_2)^+$ (53)]. HR-MS 288.0407 [calculated for $C_{11}H_6N_3O_2F_4$ = 288.0396].

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