ADDITION OF FLUORODINITROMETHANE TO SOME α,β-UNSATURATED CARBONYL COMPOUNDS

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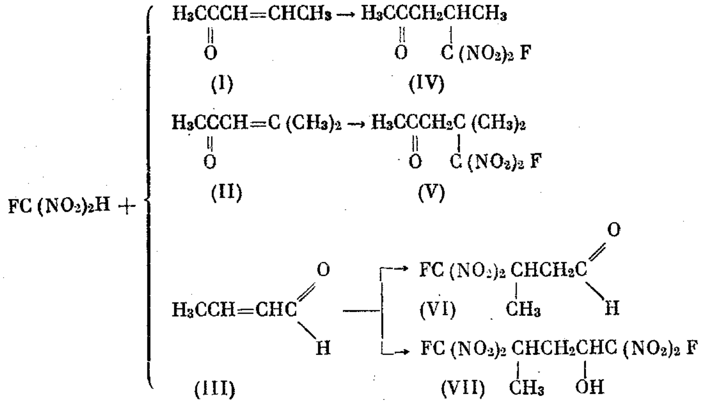
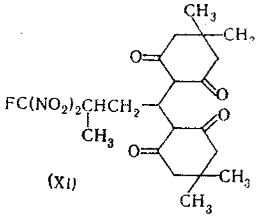
Recently it was shown that fluorodinitromethane (FDNM) easily enters into the Michael reaction with compounds containing an activated double bond [1, 2]. In a number of papers it was also established that FDNM is active in the Henry reaction with saturated aldehydes of the aliphatic series [3-5]. In direct view of these results it seemed of interest to study the behavior of FDNM in reactions with compounds containing both reactions centers: an activated double bond and a carbonyl group. For this we selected three compounds: 3-pentene-2-one (I), 4-methyl-3-pentene-2-one (II) and 2-butenal (III). (I) and (II) form with FDNM only the Michael adducts (IV) and (V), while (III) under the same conditions adds FDNM both to the double bond (VI) and to the carbonyl group (VII)

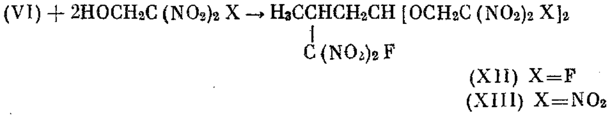


In all cases the addition of FDNM proceeds primarily at the double bond, and the carbonyl group under these conditions is less reactive than the double bond. Taking into consideration [1, 6, 7], we believe that in our case the FDNM adds to the β-carbon atom of the α,β-unsaturated compound. Compounds (IV) and (V) retain the reactivity of the carbonyl group and easily give the corresponding 2,4-dinitrophenylhydrazones (VIII) and (IX). 4,4,4-Fluorodinitro-3-methylbutanal (VI) also easily forms the 2,4-dinitrophenylhydrazone (X) and the dimedon derivative (XI)



(XI)

. The reactivity of (VI) was used by us to obtain the acetals with 2,2,2-fluorodinitroethanol (XII) and 2,2,2-trinitroethanol (XIII)



$$\text{(VI)} + 2HOCH_2C(NO_2)_2X \rightarrow H_3C\underset{\underset{C(NO_2)_2F}{|}}{C}HCH_2CH[OCH_2C(NO_2)_2X]_2$$

(XII) X=F
(XIII) $X=NO_2$

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Fluoropolynitro alcohol (VII) possesses adequate nucleophilicity and is esterified by acid chlorides. It is a thermally unstable compound and when vacuum-distilled it easily releases 1 mole of FDNM with the formation of (VI)

$$(\mathrm{VII}) \xrightarrow{\Delta} (\mathrm{VI}) + \mathrm{FC(NO_2)_2H}$$

EXPERIMENTAL

5,5,5-Fluorodinitro-4-methyl-2-pentanone (IV). To a solution of 14.9 g of FDNM [3] in 40 ml of ethanol was added 8.4 g of (I) (bp 120-122°, n_D^{20} 1.4360), and the mixture was refluxed for 8 h. After distilling off the ethanol and unreacted starting substances in vacuo at 20° the still residue was vacuum-distilled twice. We obtained 6.3 g (30.2%) of (IV) as a colorless liquid with bp 76-78° (3 mm); n_D^{20} 1.4392. Found: C 34.64; H 4.33; N 13.27; F 9.50%; mol. wt. 206. $C_6H_9O_5N_2F$. Calculated: C 34.60; H 4.36; N 13.42; F 9.13%; mol. wt. 208. The principal frequencies in the IR spectrum are (cm^{-1}): 1720 s ($\nu_{C=O}$) 1594 s ($\nu_{as\ NO_2}$), 1319 m ($\nu_{s\ NO_2}$), 1172 m (ν_{C-F}), 798 s (ν_{C-N}).

2,4-Dinitrophenylhydrazone (VIII), mp 116-117° (from ethanol). Found: C 37.35; H 3.24; N 21.61%. $C_{12}H_{13}O_8N_6F$. Calculated: C 37.11; H 3.37; N 21.65%.

5,5,5-Fluorodinitro-4,4-dimethyl-2-pentanone (V). To a solution of 37.2 g of FDNM in 80 ml of ethanol was added 19.6 g of (II) (bp 130°, n_D^{20} 1.4440), and the mixture was refluxed for 24 h. We obtained 14.33 g (32.2%) of (V) as a colorless liquid with bp 65-66° (1.5 mm); n_D^{20} 1.4480. Found: C 38.02; H 4.81; N 12.71%. $C_7H_{11}O_5N_2F$. Calculated: C 38.10; H 4.98; N 12.60%. The principal frequencies in the IR spectrum are (cm^{-1}): 1724 s ($\nu_{C=O}$), 1601 v.s. ($\nu_{as\ NO_2}$), 1320 m ($\nu_{s\ NO_2}$), 1104 m (ν_{C-F}), 799 s (ν_{C-N}).

2,4-Dinitrophenylhydrazone (IX), mp 109-110° (from ethanol). Found: C 38.76; H 3.58; N 20.75; F 4.90%; mol. wt. 387. $C_{13}H_{15}O_8N_6F$. Calculated: C 38.80; H 3.76; N 20.89; F 4.72%; mol. wt. 402.

Reaction of FDNM with 2-Butenal (III). To a solution of 39.7 g of FDNM in 100 ml of ethanol was added 22.5 g of (III) (bp 101-102°, n_D^{20} 1.4370), and the mixture was refluxed for 5 h. The reaction mass was poured into 500 ml of water and the insoluble oil was separated, after which it was dissolved in ether, and the ether solution was washed with water and dried over $MgSO_4$. After distilling off the ether and vacuum-distillation of the residue we obtained 35.4 g of a liquid reaction product, from which (VI) was isolated as a colorless liquid by repeated vacuum-distillation through a column. Yield 9.3 g; bp 46-48° (0.5-1 mm); n_D^{20} 1.4490 (supercooled liquid); mp 36-36.5° (from petroleum ether). Found: C 30.49; H 3.50; N 14.60; F 9.50%; mol. wt. 188. $C_5H_7O_5N_2F$. Calculated: C 30.93; H 3.63; N 14.43; F 9.79%; mol. wt. 194. The principal frequencies in the IR spectrum are (cm^{-1}): 1728 s ($\nu_{C=O}$), 1608 v.s. ($\nu_{as\ NO_2}$), 1319 m ($\nu_{s\ NO_2}$), 1118 w (ν_{C-F}), 799 s (ν_{C-N}).

2,4-Dinitrophenylhydrazone (X), mp 121-122° (from ethanol). Found: C 35.70; H 3.12; N 22.47; F 5.03%. $C_{11}H_{11}O_8N_6F$. Calculated: C 35.30; H 2.96; N 22.46; F 5.08%.

The dimedon derivative (XI) was obtained as white prisms with mp 155-157° (from 50% aqueous ethanol). Found: C 55.11; H 6.82; N 6.10; F 4.04%; mol. wt. 445. $C_{21}H_{29}O_8N_2F$. Calculated: C 55.25; H 6.40; N 6.14; F 4.16%; mol. wt. 456.

The viscous pale yellow oil (24.2 g, n_D^{20} 1.4652), remaining in the pot after distilling off (VI), is impure (VII). The oil was dissolved in ether, decolorized with active carbon for 24 h, the ether was evaporated, and the pure (VII) was extracted as the acetate.

1,5-Difluoro-1,1,5,5-tetranitro-4-methyl-2-pentanol Acetate (XIV). A solution of 9.54 g of (VII) (from the preceding experiment) in 56.6 ml of CH_3COCl was refluxed for 8.5 h in the presence of 3.99 g of $AlCl_3$. The CH_3COCl was removed from the reaction mass, while the residue was poured into chilled water, washed, separated from the water, dissolved in ether, and dried over $MgSO_4$. The ether solution was decolorized with active carbon, the ether was distilled off, and the residue was kept in vacuo (2 mm) at 40° for 2 h, after which it was recrystallized from a CCl_4 – n-heptane mixture (1 : 4). We obtained 5.39 g (50%) of (XIV) as colorless plates with mp 70-71°. Found: C 27.04; H 2.70; N 15.12%. $C_8H_{10}O_{10}N_4F_2$. Calculated: C 26.67; H 2.80; N 15.55%. The principal frequencies in the IR spectrum are (cm^{-1}): 1771 s ($\nu_{C=O}$), 1608 v.s. ($\nu_{as\ NO_2}$), 1312 s ($\nu_{s\ NO_2}$), 798 s (ν_{C-N}).

Thermolysis of 1,5-Difluoro-1,1,5,5-tetranitro-4-methyl-2-pentanol. In a distillation apparatus was placed 20 g of (VII) and the compound was heated in a vacuum of 0.5-1 mm. (VI), contaminated with decomposition products, slowly distilled at a bath temperature of 110-170°. The (VI) collected in the receiver was purified further by vacuum-distillation. Yield 9.6 g (78.5%); bp 59-62° (1 mm); mp 36-36.5° (from petroleum ether). The FDNM, liberated during thermolysis, was collected in a low-temperature trap and identified as 2,2,2-fluorodinitroethanol; bp 62-65° (2 mm); n_D^{20} 1.4315. From [3]: bp 62-66° (1-2 mm); n_D^{20} 1.4338. The IR spectrum was identical with the spectrum of authentic 2,2,2-fluorodinitroethanol.

Acetal of 4,4,4-fluorodinitro-3-methylbutanal with 2,2,2-Fluorodinitroethanol (XII). With stirring, 18.48 g of 2,2,2-fluorodinitroethanol was added dropwise at 19° to 19 ml of H_2SO_4 (d 1.83), after which the mixture was stirred at 35-40° until the alcohol had dissolved completely. Then the mixture was cooled to 0°, and 3.88 g of (VI) was added dropwise in 30 min at 0-5°, after which the mixture was stirred at 0° for 4 h. The obtained viscous mass was transferred to cracked ice, washed with chilled water, and filtered. We obtained 6.15 g (63.5%) of (XII) as white needles with mp 69-69.5° (from a $CHCl_3 - CCl_4$ mixture, 1 : 3). Found: C 22.27; H 2.12; N 17.75; F 12.00%; mol. wt. 481. $C_9H_{11}O_{14}N_6F_3$. Calculated: C 22.32; H 2.29; N 17.36; F 11.77%; mol. wt. 484.

Acetal of 4,4,4-Fluorodinitro-3-methylbutanal with 2,2,2-Trinitroethanol (XIII). The reaction with 21.72 g of 2,2,2-trinitroethanol was run in the same manner as in the preparation of (XII). The product, isolated as viscous oil, was purified by reprecipitation from HNO_3 (d 1.50) solution with ice water. Yield of (XIII) 1.32 g (12.3%), mp 56.5-57.5° (from CCl_4). Found: C 20.50; H 2.16; N 20.60; F 3.52%; mol. wt. 512. $C_9H_{11}O_{18}N_8F$. Calculated: C 20.08; H 2.06; N 20.82; F 3.53%; mol. wt. 538.

CONCLUSIONS

1. The addition of fluorodinitromethane to unsaturated carbonyl compounds is primarily accomplished at the double bond.

2. In the case of the reaction with 2-butenal, together with the adduct at the double bond, we also isolated the product of the addition of FDNM to both reaction centers.

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