isocyanates and isothiocyanate structure was found for dialkylarsine cyanates and thiocyanates, respectively.

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REACTIONS OF METHYL 2-IMINO-3,3,3-TRIFLUOROPROPIONATES WITH CH- AND PH-ACIDS

S. N. Osipov, V. B. Sokolov, A. F. Kolomets, I. V. Martynov, and A. V. Fokin

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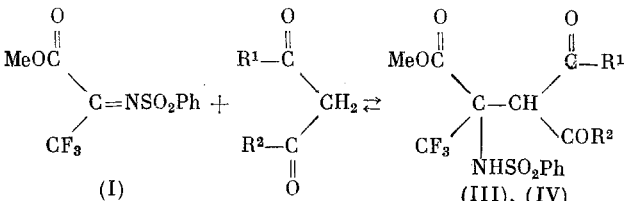
Perfluoroacylimines and sulfonylimines of hexafluoroacetone are among the strongest π-acids as seen in their reactions with O-, N- and P-nucleophiles [1] and in a number of cases, with CH-acids [2]. In the present work, we examined the behavior of methyl esters of 2-benzenesulfonylimino- and 2-trifluoroacetylimino-3,3,3-trifluoropropionates (I) and (II) which are analogs of the corresponding hexafluoroacetone derivatives, in which the CF_3 is replaced by a carbomethoxyl group, toward CH- and PH-acids.

Benzenesulfonylimine (I) in CH_2Cl_2 undergoes an equilibrium reaction with diethyl malonate and acetylacetone at 20°C to give the C-alkylation products (III) and (IV) in 20-30% yield. The equilibrium is attained more rapidly upon heating but its position is virtually unaltered.



(I)

$R^1 = R^2 = EtO$(III), $R^1 = R^2 = Me$(IV).

The reaction of imine (II) with diethyl malonate is even more difficult and the C-alkylation product (V) may be obtained in 30% yield only upon acid catalysis. On the other hand, imine (II) reacts with acetylacetone and ethyl acetoacetate at 20°C to give adducts (VI) and (VII) in high yield, which is likely due to a strong shift in the equilibrium as a result of the stabilization of their enol forms.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Institute of Physiologically Active Compounds, Academy of Sciences of the USSR, Chernogolovka.

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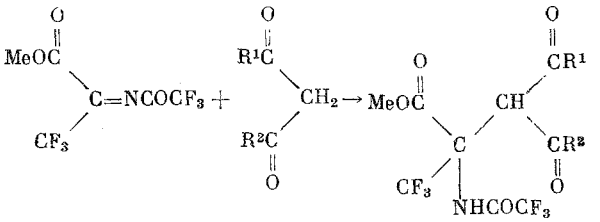
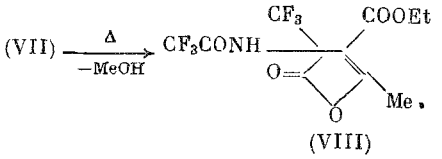


(II) (V) — (VII)

$R^1 = R^2 = EtO$(V); $R^1 = R^2 = Me$(VI); $R^1 = Me$, $R^2 = EtO$(VII).

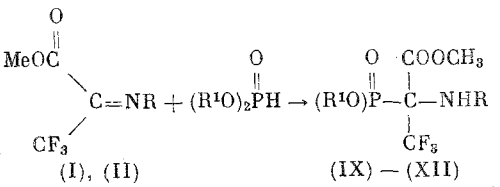
This is indicated by the facile lactonization of (VII) upon heating.



(VIII)

However, it is not excluded that acetylacetone and ethyl acetoacetate react with imine (II) in the enol form through an asymmetrical ($2\pi + 2\pi$) transition state.

In contrast to CH-acids, PH-acids uniformly react readily with imines (I) and (II) almost quantitatively to form phosphonates (IX)-(XII).



(I), (II) (IX) — (XII)

$R = PhSO_2$, $R^1 = Me$(IX); $R = PhSO_2$, $R^1 = Et$(X); $R = CF_3CO$, $R^1 = C_5H_{11}$(XI); $R = CF_3CO$, $R^1 = Ph$(XII).

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra (δ, ppm) were taken on a Bruker CXP-200 spectrometer in $(CD_3)_2CO$ for (III)-(VIII), (XI), and (XII) and in $CDCl_3$ for (IX) and (X) relative to TMS as an internal standard and CF_3CO_2H as an external standard. The IR spectra were taken on a UR-20 spectrometer.

Methyl 2-trifluoromethyl-2-benzenesulfamido-3-carboethoxysuccinate (III). A solution of 1.3 g diethyl malonate in 5 ml CH_2Cl_2 was added at 20°C to a solution of 2.2 g imine (I) in 5 ml CH_2Cl_2. The mixture was maintained for 48 h and the crystalline precipitate was filtered off and washed with hexane to give 0.8 g (22%) ester (III), mp 82-84°C. PMR spectrum 1.22 t (6H, $2CH_3$, $^2J_{H-H}$ = 7.0 Hz), 3.86 s (3H, CH_3O), 4.10 m (4H, CH_2O), 7.40-7.98 m (6H, Ph, NH). ^{19}F NMR spectrum: −9.3 s (CF_3). Found: C, 44.56; H, 4.02; N, 3.33%. Calculated for $C_{17}H_{20}F_3NO_8S$: C, 44.83; H, 4.39; N, 3.08%.

Ester (III) was obtained in 20, 22 and 21% yields after three, four and five days, respectively.

Methyl 2-Trifluoromethyl-2-benzenesulfamido-3-acetyl-4-one-pentanoate (IV). A mixture of 2.3 g imine (I) and 3 ml acetylacetone was heated for 4 h at 90°C and cooled. The crystalline precipitate was filtered off and washed with CCl_4 to give 0.9 g (30%) ester (IV), mp 84-86°C. PMR spectrum: 2.53 s (6H, $2CH_3$), 3.83 s (3H, OCH_3), 5.07 s (1H, CH), 7.3-8.00 m (6H, C_6H_5, NH). ^{19}F NMR spectrum: −9.7 s (CF_3). Found: C, 45.44; H, 4.17; H, 3.52%. Calculated for $C_{15}H_{16}F_3NO_6S$: C, 45.56; H, 4.05; N, 3.54%.

Ester (IV) was obtained in 29 and 30% yield after 8 and 16 h, respectively.

Methyl 2-Trifluoromethyl-2-trifluoroacetylamino-3-carboethoxysuccinate (V). A mixture of 5.0 g imine (II), 3.1 g diethyl malonate and 0.03 g p-toluenesulfonic acid was heated for 3 h at 90°C and fractionated to give 2.7 g (30%) ether (V), bp 103°C (1 mm Hg), n_D^{25} 1.3950.

PMR spectrum: 1.27 m (6H, $2CH_3$), 3.82 s (3H, OCH_3), 4.19 s (1H, CH), 4.24 m (4H, OCH_2), 8.68 s (1H, NH). ^{19}F NMR spectrum: −8.68 s (CF_3), −1.51 s (CF_3). Found: C, 37.83; H, 3.26; N, 3.67%. Calculated for $C_{13}H_{15}F_6NO_7$: C, 37.95; H, 3.64; N, 3.40%.

Methyl 2-Trifluoromethyl-2-trifluoroacetylamino-3-acetyl-4-one-pentanoate (VI). A mixture of 5.0 g imine (II) and 2.0 g acetylacetone was maintained for 24 h at 20°C. The solid product was crystallized from CCl_4 to give 6.5 g (92%) ester (VI), mp 97-98°C. PMR spectrum: 2.34 s (3H, CH_3), 2.37 s (3H, CH_3), 3.80 s (3H, OCH_3), 5.02 s (1H, CH), 9.25 br. s (1H, NH). ^{19}F NMR spectrum: −1.7 s (CF_3), −8.4 s (CF_3). Found: C, 37.48; H, 3.50; N, 4.20%. Calculated for $C_{11}H_{11}F_6NO_5$: C, 37.60; H, 3.13; N, 3.98%.

Methyl 2-Trifluoromethyl-2-trifluoroacetylamino-3-acetylsuccinate (VII). By analogy to (VI), 4.7 g imine (II) and 2.4 g ethyl acetoacetate gave 5.6 g (78%) ester (VII), bp 100°C (1 mm Hg), n_D^{25} 1.3993. PMR spectrum: 1.25 t and 1.26 t (3H, CH_3, $^2J_{H-H}$ = 7.0 Hz), 2.26 s and 2.27 s (3H, CH_3), 3.80 s and 3.81 s (3H, OCH_3), 4.20 m (2H, OCH_2), 4.55 s and 4.57 s (1H, CH), 8.50 s and 8.70 s (1H, NH). ^{19}F NMR spectrum: −8.16 s and −7.04 s (CF_3), −1.59 s and −1.55 s (CF_3). Found: C, 37.50; H, 3.20; N, 3.89%. Calculated for $C_{12}H_{13}F_6NO_6$: C, 37.79; H, 3.41; N, 3.67%.

3-Trifluoromethyl-3-trifluoroacetylamino-4-carboethoxy-5-methylfuran-2-one (VIII). A mixture of 3.5 g imine (II) and 1.8 g ethyl acetoacetate was heated at 100°C for 6 h and cooled. The crystalline precipitate was washed with CCl_4 to give 1.5 g (31%) furanone (VIII), mp 128-129°C. PMR spectrum: 1.15 m (3H, CH_3), 2.50 m (3H, CH_3), 4.11 m (2H, OCH_2), 7.12 m (1H, NH). ^{19}F NMR spectrum: −8.21 s and −7.09 s (CF_3), −1.70 s and −1.63 s (CF_3). Found: C, 37.60; H, 2.16; N, 4.06%. Calculated for $C_{11}H_9F_6NO_5$: C, 37.82; H, 2.56; N, 4.01%.

Methyl 2-benzenesulfamido-2-dimethoxyphosphoryltrifluoropropionate (IX). A solution of 1.2 g dimethyl phosphite in 5 ml CH_2Cl_2 was added to a solution of 3.0 g imine (I) in 5 ml CH_2Cl_2. The mixture was maintained for 24 h at 20°C. The crystalline precipitate was filtered and washed twice with hexane to give 3.5 g (85%) ester (IX), mp 121°C. PMR spectrum: 3.75 m (6H, $2CH_3$), 3.80 s (3H, OCH_3), 7.66 m (3H, C_6H_5), 7.98 m (2H, C_6H_5), 8.10 br. s (1H, NH). ^{19}F NMR spectrum: 10.77 d (CF_3, J = 5.0 Hz). Found: C, 35.77; H, 3.70; N, 3.59%. Calculated for $C_{12}H_{15}F_3NO_7PS$: C, 35.55; H, 3.70; N, 3.45%.

Methyl 2-Benzenesulfamido-2-diethoxyphosphoryltrifluoropropionate (X). By analogy to the procedure for the preparation of (IX), 3.1 g imine (I) and 1.4 g diethyl phosphite gave 3.8 g (80%) ester (X), mp 80-81°C. PMR spectrum: 1.25 m (6H, $2CH_3$), 3.75 s (3H, OCH_3), 4.18 m (4H, $2\cdot CH_2$), 7.68 m (3H, C_6H_5), 7.94 m (2H, C_6H_5), 8.11 s (1H, NH). ^{19}F NMR spectrum: 11.05 d (CF_3, J = 5.0 Hz). Found: C, 38.69; H, 4.40; N, 3.18%. Calculated for $C_{14}H_{19}F_3NO_7\cdot$ PS: C, 38.79; H, 4.38; N, 3.23%.

Methyl 2-Trifluoroacetamido-2-diamyloxyphosphoryltrifluoropropionate (XI). A solution of 3.2 g imine (II) in 5 ml CH_2Cl_2 was added to a solution of 2.6 g diamyl phosphite in 5 ml CH_2Cl_2. The mixture was heated at reflux for 6 h and the solvent was removed in vacuum. The crystalline product was heated with pentane to give 3.1 g (51%) ester (XI), mp 53.55°C. PMR spectrum: 0.93 m (6H, $2CH_3$), 1.33 m (8H, $2C_2H_4$), 1.60 m (4H, $2CH_2$), 3.80 s (3H, OCH_3), 4.16 m (4H, $2OCH_2$), 8.55 m (1H, NH). ^{19}F NMR spectrum: −11.48 d (CF_3, J = 4.8 Hz), −3.02 s (CF_3). Found: C 40.37; H, 5.20; N, 3.02%. Calculated for $C_{16}H_{26}F_6NO_6P$: C, 40.59; H, 5.49; N, 2.95%.

Methyl 2-Trifluoroacetamido-2-diphenyloxyphosphoryltrifluoropropionate (XII). By analogy to the preparation of (XI), 2.0 g imine (II) and 1.6 g diphenyl phosphite gave 1.5 g (50%) ester (XII), mp 86-87°C. PMR spectrum: 3.75 s (3H, OCH_3), 7.25 m (10H, $2C_6H_5$), 7.60 m (1H, NH). ^{19}F NMR spectrum: −11.93 d (CF_3, J = 4.4 Hz), −2.72 s (CF_3). Found: C, 44.81; H, 2.50; N, 2.12%. Calculated for $C_{18}H_{14}F_6NO_6P$: C, 44.53; H, 2.06; N, 2.06%.

CONCLUSION

1. 2-Iminotrifluoropropionates undergo equilibrium reactions with strong CH-acids. The position of the equilibrium is highly dependent on the structure of both the imine and the CH-acid.

2. A mild, almost quantitative addition of dialkyl and diaryl phosphites at the C=N bond of 2-iminotrifluoropropionates was developed.

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