Chemistry

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Abstract

Full Text

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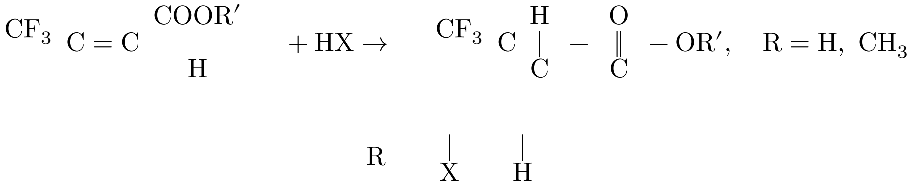
CONJUGATION OF BONDS IN 1,1-BIS(TRIFLUOROMETHYL)-2-NITROETHYLENE AND HEXAFLUOROISOPROPYLIDENEMALONIC ESTER

The trifluoromethyl group is one of the strong electron-withdrawing substituents. A comparison of the electron-acceptor strength of the trifluoromethyl group and other negative groups can be made by studying the direction of heterolytic addition of unsymmetrical molecules to a carbon–carbon double bond polarized under the action of a trifluoromethyl group on one side and another negative group on the other side. It is known that the addition of nucleophilic and electrophilic reagents to γ, γ, γ-trifluorocrotonic acid or its ester proceeds in such a way that the negative part of the addend molecule is directed to the β-position with respect to the carboxyl or carbalkoxy group (^{1}).

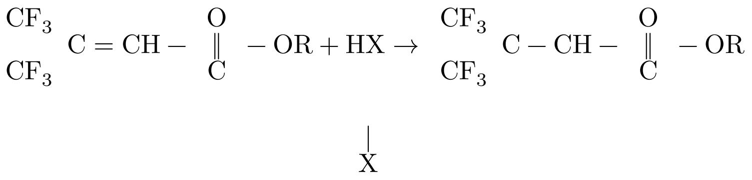
A similar direction of addition is also observed in the case of the ester of β-methyl-γ, γ, γ-trifluorocrotonic acid (^{2}):



$$\begin{array}{l} CF_3\ C=C\begin{matrix}COOR'\\ \\H\end{matrix} \quad + HX \rightarrow \quad CF_3\ C\begin{matrix}H\\|\\C\end{matrix} - \begin{matrix}O\\\|\\C\end{matrix} - OR', \quad R=H,\ CH_3 \\ \qquad\qquad\qquad\qquad\qquad R \quad \begin{matrix}|\\X\end{matrix} \quad \begin{matrix}|\\H\end{matrix} \end{array}$$

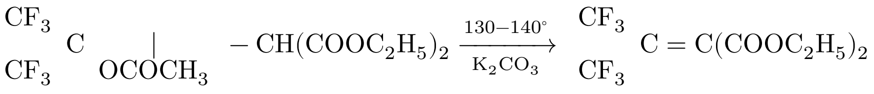
Thus, the carboxyl group proves to be a stronger electron-acceptor substituent than the trifluoromethyl group.

However, in the case where a carboxyl or carbalkoxy group competes with two trifluoromethyl groups, the polarization of the double bond is reversed: as a result of the addition of various reagents to hexafluorodimethylacrylic acid or its ester, α-substituted derivatives of β,β-bis(trifluoromethyl)propionic acid are obtained; the influence of two electron-acceptor trifluoromethyl groups on the polarization of the double bond proves stronger than the influence of one carbalkoxy group (^{2}):



$$\begin{array}{l}CF_3\\CF_3\end{array}C=CH-\overset{O}{\overset{\|}{C}}-OR+HX\rightarrow\begin{array}{l}CF_3\\CF_3\end{array}\underset{\underset{X}{|}}{C}-CH-\overset{O}{\overset{\|}{C}}-OR$$

In this connection it was of interest to trace the competing influence of two trifluoromethyl groups on one side and two carbalkoxy groups or one nitro group on the other. The corresponding unsaturated compounds were obtained by us in the study of reactions of hexafluoroacetone and subsequent transformations of the substances formed (^{3}). By low-temperature pyrolysis of β-acetoxyhexafluoroisopropylmalonic ester in the presence of a catalytic amount of potassium carbonate, hexafluoroisopropylidenemalonic ester (I) was obtained:



$$\begin{array}{l}CF_3\\CF_3\end{array}C\underset{OCOCH_3}{|}-CH(COOC_2H_5)_2\xrightarrow[K_2CO_3]{130-140^\circ}\begin{array}{l}CF_3\\CF_3\end{array}C=C(COOC_2H_5)_2$$

(I)

By the interaction of hexafluoroacetone with nitromethane in the presence of potassium hydroxide, 1,1-bis(trifluoromethyl)-2-nitroethanol (II) was synthesized, which upon treatment with ketene gives the corresponding acetate (III). Upon distillation of this ···

acetate in the presence of catalytic amounts of potassium, 1,1-bis(trifluoromethyl)-2-nitroethylene (IV) is readily formed. The preparation of other fluorinated

$$(CF_3)_2C{=}O+CH_3NO_2\xrightarrow[K_2CO_3]{\sim 120^\circ}(CF_3)_2C(OH)CH_2NO_2\xrightarrow{CH_2{=}C{=}O}(CF_3)_2C(OCOCH_3)CH_2NO_2$$

(II) (III)

$$(CF_3)_2C(OCOCH_3)CH_2NO_2\xrightarrow[K_2CO_3]{130^\circ-140^\circ}(CF_3)_2C{=}CHNO_2$$

(IV)

nitroolefins by this method has already been described in the literature $^{(4)}$.

The reaction of hexafluoroisopropylidenemalonic ester with ammonia leads to the formation of α-aminohexafluoroisopropylmalonic ester (V). The structure of this ester was proved by its saponification and decarboxylation to the previously known $^{(3)}$ hexafluorovaline (VI)

$$(CF_3)_2C{=}C(COOC_2H_5)_2 \xrightarrow{NH_3} (CF_3)_2CH{-}C(NH_2)(COOC_2H_5)_2 \longrightarrow (CF_3)_2CH{-}CH(NH_2){-}COOH$$

(V) (VI)

Indirect evidence for the structure of ester V is also the ease of saponification of the trifluoromethyl groups in this compound, which is evidently caused by the presence of a hydrogen atom at the carbon atom bonded to the trifluoromethyl group (cf. (3)).

From these data it follows that two trifluoromethyl groups, in their effect on the polarization of an olefinic double bond, successfully compete not only with one but also with two carbalkoxy groups.

In the reaction of 1,1-bis(trifluoromethyl)-2-nitroethylene (IV) with nucleophilic reagents, an order of addition opposite to the usual one is also observed. However, the anion (VII) formed is stabilized not by addition of a proton, but by expulsion of the nitrite ion, as occurs in the case of analogous reactions of 1,2-dinitroolefins (6); the final result of the reaction is substitution of the nitro group by a new group:

$$(CF_3)_2C{=}CHNO_2 \xrightarrow{+X^{\ominus}} [(CF_3)_2C^{\ominus}{-}C(H)(NO_2)X] \xrightarrow{-NO_2^{\ominus}} (CF_3)_2C{=}CHX$$

(VII)

Thus, reactions with 2,4-dinitrophenylhydrazine and with aniline lead to formation of the corresponding substitution products, VIII and IX, respectively, which probably exist in tautomeric forms: 2,4-dinitrophenylhydrazone of bis-trifluoromethylacetaldehyde (VIIIa) and anil of bis-trifluoromethylacetaldehyde (IXa). Saponification of the anil with dilute HCl and subsequent treatment of the reaction mixture with 2,4-dinitrophenylhydrazine gave dinitrophenylhydrazone identical with VIIIa:

$$(CF_3)_2C{=}CHNO_2 \xrightarrow{O_2N{-}C_6H_3(NO_2){-}NHNH_2} (CF_3)_2C{=}CHNHNH{-}C_6H_3(NO_2)_2 \rightleftharpoons (CF_3)_2CH{-}CH{=}NNH{-}C_6H$$

(VIII) (VIIIa)

$$(CF_3)_2C{=}CHNO_2 \xrightarrow{C_6H_5NH_2} (CF_3)_2C{=}CH{-}NH{-}C_6H_5 \rightleftharpoons (CF_3)_2CH{-}CH{=}N{-}C_6H_5 \longrightarrow [(CF_3)_2CH{-}C$$

(IX) (IXa)

$$[(CF_3)_2CH{-}CHO] \xrightarrow{O_2N{-}C_6H_3(NO_2){-}NHNH_2} (CF_3)_2CH{-}CH{=}NNH{-}C_6H_3(NO_2)_2$$

schematic structures A and B

Figure 1: schematic structures A and B

Summarizing the results, it may be said that the influence of two trifluoromethyl groups located at one of the two carbon atoms joined by a double bond on the order of addition proves to be more

stronger than could be expected from a simple summation of the effects of each trifluoromethyl group. Indeed, in the presence of one trifluoromethyl group on one side and one carboxyl group on the other side of the olefinic bond, a greater displacement of the π-electrons toward the carbalkoxy group is observed, whereas two trifluoromethyl groups withdraw the π-electrons more strongly than two carbalkoxy groups (see A). This phenomenon evidently occurs as a result of disturbance of the coplanarity of two bulky carbalkoxy groups (see B):

Experimental Part

Hexafluoroisopropylidenemalonic ester (I).
14.5 g of β-acetoxyhexafluoroisopropylmalonic ester (4) and 0.3 g of potash were placed in a Claisen flask fitted with a descending condenser and heated on a Wood' s-metal bath for 2 hours (bath temperature 130-140°). The distillate was washed with saturated sodium bicarbonate solution, then with water, and dried with magnesium sulfate. Distillation gave 10.6 g (87.6% of theory) of hexafluoroisopropylidenemalonic ester, b.p. 59-60°/6 mm, n_D^{20} 1.3720; d_4^{20} 1.3025; found MR 53.74; calculated for $C_{10}F_6H_{10}O_4$ 52.09.

$C_{10}F_6H_{10}O_4$. Found, %: C 38.05; 38.25; H 3.05; 3.02; F 36.00; 36.35
Calculated, %: C 38.96; H 3.24; F 37.04

IR spectrum: $\gamma_{\max}$ 1700 cm^{-1}—absorption of the olefinic bond (^{6}).

Hexafluoroisopropylidenemalonic ester decolorizes a neutral aqueous solution of potassium permanganate.

1,1-Bis-(trifluoromethyl)-2-nitroethanol (II).
In a steel autoclave of 250 ml capacity were placed 69.0 g of nitromethane and 0.19 g of potash. On cooling with dry ice and acetone, 51.9 g of hexafluoroacetone was added. The mixture was heated at 120° for 10-12 hours. After removal of unreacted nitromethane by distillation, 55.1 g (78.4% of theory) of 1,1-bis-(trifluoromethyl)-2-nitroethanol was isolated, b.p. 67-68°/80 mm, n_D^{20} 1.3401; d_4^{20} 1.6597; found [[unclear: MR value]] 28.34; calculated for $C_4F_6H_3O_3N$ 28.65.

$C_4F_6H_3O_3N$. Found, %: C 21.12; 21.22; H 1.37; 1.43; F 49.46; 48.42; N 6.96; 7.13
Calculated, %: C 21.15; H 1.32; F 50.22; N 6.16

IR spectrum: $\gamma_{\max}$ 3400 cm^{-1}—absorption of the hydroxyl group (^{7}); $\gamma_{\max}$ 1580 cm^{-1}—absorption of the nitro group (^{7}).

Acetate of 1,1-bis-(trifluoromethyl)-2-nitroethanol (III). Through 9.3 g of 1,1-bis-(trifluoromethyl)-2-nitroethanol a large excess of ketene was passed at room temperature. Distillation in vacuo yielded 8.3 g (75.5% of theory) of the acetate, b.p. 60-62°/20 mm, n_D^{20} 1.3575; d_4^{20} 1.5368; found MR 38.56; calculated for $C_6F_6H_5O_4$ 39.34.

$C_6F_6H_5O_4N$. Found, %: C 27.25; 27.33; H 2.00; 2.10; F 40.56; 40.26
Calculated, %: C 26.77; H 1.86; F 42.37

IR spectrum: $\gamma_{\max}$ 1580 cm^{-1}—absorption of the nitro group (^{7}); $\gamma_{\max}$ 1800 cm^{-1}—absorption of the ester group (^{6}).

1,1-Bis-(trifluoromethyl)-2-nitroethylene (IV). 20.3 g of the acetate of 1,1-bis-(trifluoromethyl)-2-nitroethanol and 0.03 g of potash were placed in a Claisen flask fitted with a descending condenser and heated on a Wood' s-metal bath for 2 hours (bath temperature 110-140°). The distillate was redistilled (b.p. 70-100°), washed with water, and dried with calcium chloride. Distillation gave 8.9 g (57% of theory) of the olefin,

b.p. 93-94°, n_D^{19} 1.3355; d_4^{20} 1.5637; found MR 26.60; calculated for $C_4F_6HO_2N$ 27.69.

$C_4F_6HO_2N$.	Found, %:	C 23.20; 23.27;	H 0.66; 0.60;	F 54.32; 54.67
	Calculated, %:	C 22.96;	H 0.48;	F 54.54

IR spectrum: $\nu_{\max}$ 1700 cm^{-1}—absorption of the olefinic double bond (^{6}). 1,1-Bis(trifluoromethyl)-2-nitroethylene is a yellow liquid with a sharp unpleasant odor, a strong lacrimator; it decolorizes a neutral solution of potassium permanganate.

α-Aminohexafluoroisopropylmalonic ester (V). A solution of 7.5 g of hexafluoroisopropylidenemalonic ester in 15 ml of absolute ether was treated with 5.7 g of gaseous ammonia. The precipitated ammonium fluoride was removed by filtration, the solvent was distilled off from the filtrate, and the residue was distilled. This gave 4.2 g (53.1% of theory) of α-aminohexafluoroisopropylmalonic ester, b.p. 60-61°/1 mm, n_D^{20} 1.3840; d_4^{20} 1.4534; found MR 54.90; calculated for $C_{10}F_6H_{13}O_4N$ 52.20.

$C_{10}F_6H_{13}O_4N$.	Found, %:	C 37.35; 37.02;	H 4.15; 3.89;	F 37.51; 37.45;	N 4.45; 4.58
	Calculated, %:	C 36.92;	H 4.00;	F 35.07;	N 4.30

When α-aminohexafluoroisopropylmalonic ester was boiled with an excess of 25% KOH solution for 7 hours, 63% of the fluorine contained in the substance was mineralized.

Hexafluorovaline (VI). 0.65 g of α-aminohexafluoroisopropylmalonic ester was boiled with 2.5 ml of conc. HCl for 7 hours. The reaction mixture was evaporated to dryness, the residue was dissolved in absolute alcohol, and several drops of pyridine were added to the resulting solution. This gave 0.2 g (47.6%) of hexafluorovaline, m.p. 206–207° (decomp.), giving no depression with an authentic sample (^{2}).

2,4-Dinitrophenylhydrazone of bis(trifluoromethyl)acetaldehyde (VIIIa). 1.3 g of 1,1-bis(trifluoromethyl)-2-nitroethylene was shaken at room temperature with a solution of 1.3 g of 2,4-dinitrophenylhydrazine in a mixture of 8 ml of conc. H_2SO_4, 40 ml of water, and 5 ml of alcohol.

The precipitated solid was separated and recrystallized from heptane. Yield 1.3 g (59% of theory). M.p. 117-118°.

$C_{10}F_6H_6O_4N_4$.	Found, %:	C 33.05; 33.05;	H 1.72; 1.75;	F 31.68; 31.25;	N 15.55; 15.65
	Calculated, %:	C 33.34;	H 1.68;	F 31.65;	N 15.56

Anil of bis(trifluoromethyl)acetaldehyde (IXa). 4.0 g of 1,1-bis(trifluoromethyl)-2-nitroethylene was dissolved in 3 ml of absolute ether and, with cooling by dry ice in acetone, 1.78 g of aniline was slowly added; the temperature of the mixture was slowly brought to room temperature—during this a vigorous evolution of nitrogen oxides was observed. To complete the reaction, the solution was boiled on a water bath with a reflux condenser for 30 min. After washing with water, drying over calcium chloride, removal of the solvent, and vacuum distillation, 2.9 g (60.4% of theory) of the Schiff base was obtained, b.p. 81-82°/5 mm, n_D^{20} 1.4781; d_4^{20} 1.4016.

$C_{10}F_6H_7N$.	Found, %:	C 86.68; 46.76;	H 2.76; 2.78;	F 43.02; 42.65;	N 6.01; 6.10
	Calculated, %:	C 47.05;	H 2.74;	F 44.70;	N 5.49

On treatment of the obtained anil with 2,4-dinitrophenylhydrazine in the presence of conc. HCl, hydrazone VIIIa is formed, m.p. 117–118°, giving no depression with an authentic sample.

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Note: Figure translations are in progress. See original paper for figures.