# REACTION OF TRIFLUOROACETYL

## ISOCYANATE WITH SCHIFF BASES

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In continuation of studying the reactions of acyl isocyanates with compounds that contain a C = N bond, we studied the reaction of trifluoroacetyl isocyanate (I) with some Schiff bases, which lead to the formation of 4-oxo-2, 3-dehydro-4H-1, 3, 5-oxadiazines (IIa-f). The structure of (IIa-f) was established on the basis of the elemental analysis and IR spectral data, and via a study of their chemical properties.

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Since the IR spectra of compounds (IIa-f) are similar  $[1670-1690 (C = O) \text{ and } 1610-1625 \text{ cm}^{-1} (C = N)]$ , we subjected (IIa) and (IIc) to acid hydrolysis. The hydrolysis proceeds easily to give benzaldehyde, p-nitrobenzaldehyde, and substituted ureas (IIIa, c), which were also obtained by an independent route from (I) and anilines. The IR spectra of (IIIa, c) have the bands: 1610-1625, 1698-1725 (C = O), 3275, 3340 \text{ cm}^{-1} (NH).

 $F_{3}C \xrightarrow{O} C_{6}H_{4}X-p \xrightarrow{H_{4}O} p-XC_{6}H_{4}CHO + CF_{3}CONHCONHC_{6}H_{4}Y-p \xrightarrow{(IIIa, c)} (IIIa, c)$ 

To confirm the structure of (II) we studied the reaction of the obtained adducts with  $CH_3OH$ . From the literature it is known that 2,3-dehydrooxazin-4-ones react with  $CH_3OH$  [1,2]. The reaction of (IIa) and (IIb) with  $CH_3OH$  gave the substituted 4-oxo-perhydro-1,3,5-oxadiazines (IVa,b). The IR spectra respectively have the bands 1660-1679 (C = O), 3320 (NH) cm<sup>-1</sup> [for (IVa), and 1690, 3270 cm<sup>-1</sup> for (IVb)]. NMR spectrum ( $\delta$ , ppm): 2.19 s (CH); 3.01 (CH<sub>3</sub>O).

Instead of the expected cyclic product, the reaction of (IIf) with  $CH_3OH$  gave a linear product with a 1:2 composition. Its IR spectrum has the bands of the stretching vibrations of the C = N bond at 1620 cm<sup>-1</sup>, and broad absorption bands in the 3550-3640 cm<sup>-1</sup> region, which we attributed to the absorption of the OH groups, while bands are absent in the 1630-1800 cm<sup>-1</sup> region, which could be attributed to the absorption of the C = O group. On the basis of the IR spectral data we assume that the obtained product exists in the lactim form (Vf). Judging by the IR spectral data, the linear product with the structure of (VII), which could be obtained by cleavage of the ring C - N bond, was not obtained.

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#### EXPERIMENTAL METHOD

The IR spectra were taken as Nujol mulls on a UR-20 instrument. The NMR spectrum of (IVa) was taken on a Varian T-60 instrument in  $CHCl_3$  solution. All of the reactions of (I) with the Schiff bases were run under the same conditions as described below.

5,6-Diphenyl-4-oxo-2-trifluoromethyl-2,3-dehydro-4H-1,3,5-oxadiazine (IIa). With a vigorous stirring, a solution of 0.79 g of benzalaniline in 10 ml of abs. ether was added in drops to 0.61 g of (I) in 10 ml of abs. ether. A precipitate deposited instantly, which was filtered and washed with abs. ether. The yield was 1.11 g (80%), mp 175-180° (decompn.). Found: C 60.15; H 3.48%. C<sub>16</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>F<sub>3</sub>. Calculated: C 60.00; H 3.43%. The yields and melting points of the obtained compounds (IIb-f), and also the analysis results, are given in Table 1.

The hydrolysis of (IIa, c) was run as described in [3]. The yield of (IIIa) was 96%, mp 215-216° (decompn). Found: C 49.58; H 3.00%.  $C_{9}H_{7}N_{2}O_{2}F_{3}$ . Calculated: C 49.76; H 2.76%.

The yield of (IIIc) was 97.5%, mp 290° (decompn.). Found: C 38.90; H 2.05; N 15.13%.  $C_9H_6N_3O_4F_3$ . Calculated: C 38.98; H 2.16; N 15.16%. The independent synthesis of ureas (IIIa, c) was run as described in [3], and the yields were ~ 100%. The samples obtained by the different methods failed to depress the mixed melting points and had identical IR spectra.

5,6-Diphenyl-4-oxo-2-trifluoromethyl-2-methoxyperhydro-1,3,5-oxadiazine (IVa). To a solution of 0.45 g of (IIa) in 5 ml of abs. ether was added 0.046 g of MeOH. White crystals deposited in 2 h, which were filtered and washed with ether. The crystals are insoluble in water and in 2 N Na<sub>2</sub>CO<sub>3</sub> solution. The yield of (IVa) was 0.39 g (80%), mp 198-200°. Found: C 57.62; H 4.20%.  $C_{17}H_{15}N_2O_3F_3$ . Calculated: C 57.95; H 4.26%.

Com- pound	Yield, %	mp, °C	Found,%			Empirical	Calculated,%		
			с	н	N	formula	с	н	N
(IIb) (IIc) * (IId)	78 62 77	159	58,62 47,03 59,68	$3,80 \\ 2,48 \\ 4,72$	8,00 11,28	C <sub>17</sub> H <sub>13</sub> N <sub>2</sub> O <sub>4</sub> F <sub>3</sub> C <sub>15</sub> H <sub>9</sub> N <sub>4</sub> O <sub>4</sub> F <sub>3</sub> C <sub>18</sub> H <sub>12</sub> N <sub>3</sub> O <sub>2</sub> F <sub>3</sub>	$58,28 \\ 46,83 \\ 59,50$	$3,71 \\ 2,19 \\ 4,40$	8,03 11,57
(IIe) (IIf)	81 89	178—179 185—190 (decom.)	${}^{62,31}_{54,05}$	2,63 2,78	11,54	$\substack{C_{16}H_{10}N_3O_4F_3\\C_{16}H_{10}N_2O_2ClF_3}$	$62,46 \\ 54,16$	2,74 2,74	11,50

TABLE 1. 5,6-Diaryl-4-oxo-2-trifluoromethyl-2,3-dehydro-4H-1,3,5-oxadiazines (IIb-f)

\* Solvent = CHCl<sub>2</sub>.

 $\frac{6-p-Methoxyphenyl-5-phenyl-4-oxo-2-trifluoromethyl-2-methoxyperhydro-1, 3, 5-oxadiazine (IVb).}{To a solution of 1.13 g of (IIb) in 10 ml of abs. ether was added 0.1 g of MeOH. The mixture was heated at 50° for 6 h, after which pale yellow crystals deposited. The yield of (IVb) was 1.04 g (85%), mp 180-182°. Found: C 61.61; H 4.72%. C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>O<sub>4</sub>F<sub>3</sub>. Calculated: C 61.71; H 4.85%.$ 

Reaction of (III) with CH<sub>3</sub>OH. To 0.2 g of (IIf) was added 3 ml of MeOH, and then the mixture was heated at  $50-60^{\circ}$  for 8 h. The excess alcohol was removed in vacuo. We obtained 0.16 g (69% yield) of (Vf) as crystals with mp 188-192° and 194-195° (from CHCl<sub>3</sub>), which are readily soluble in water and in 2 N Na<sub>2</sub>CO<sub>3</sub> solution. Found: C 51.61; H 4.18%. C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>ClF<sub>3</sub>. Calculated: C 51.71; H 4.05%.

### CONCLUSIONS

Trifluoroacetyl isocyanate reacts with Schiff bases on the type of 2 + 4-cycloaddition to give substituted 4-oxo-1, 3, 5-oxadiazines.

### LITERATURE CITED

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