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# PREPARATION OF N-SUBSTITUTED HEXAFLUOROISOPROPYLIDENIMINES

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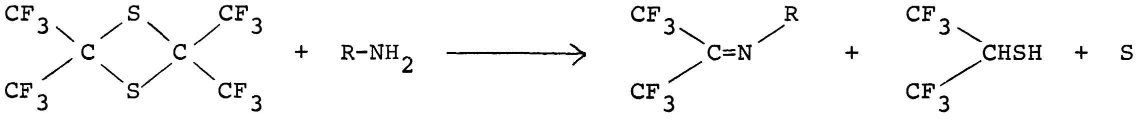
N-Substituted hexafluoroisopropylidenimines were synthesized from hexafluorothioacetone dimer [1] by treatment with either aryl- or alkylamines. The phenylhydrazone and semicarbazone of hexafluoroacetone were also obtained directly from 1 and carbonyl reagents.

Hexafluoroisopropylidenimine [2, R=H] and its N-substituted derivatives appear to be useful intermediates for the syntheses of hexafluoroisopropyl compounds. Although Middleton et al.[1,2] have prepared the imine and its N-methyl derivative by the reaction of hexafluoroacetone with either ammonia or methylamine followed by dehydration of the resulting adducts, present knowledge of the experimental conditions for preferential elimination of water from adducts of hexafluoroacetone with other amines are far from satisfactory.

On the other hand, Zeifman et al.[3] prepared N-phenylhexafluoroisopropylidenimine [2, R=Ph] by a Wittig-like reaction, which involved the reaction of hexafluoroacetone with phenylisocyanate in the presence of triphenylphosphine oxide as catalyst. Furthermore, they prepared the oxime and semicarbazone of hexafluoroacetone by elimination of aniline from the corresponding adducts obtained from condensation of N-phenylhexafluoroisopropylidenimine with hydroxylamine[4] and semicarbazide[5] respectively.

We now describe a convenient general method for the preparation of these N-substituted hexafluoroisopropylidenimines. Hexafluorothioacetone is an unstable gas which dimerizes very readily into 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane [1]. This stable dimer, bp 110°C, can be prepared directly from hexafluoropropene and sulfur in sulfolan[6]. Our studies of the nucleophilic reactions on this dimer have revealed that at room temperature, both aryl- and alkylamines reacted in polar solvents with liberation of sulfur. Among the various solvents used, dimethylformamide was the most effective in promoting reaction. The reaction appears to proceed according to the following equation:

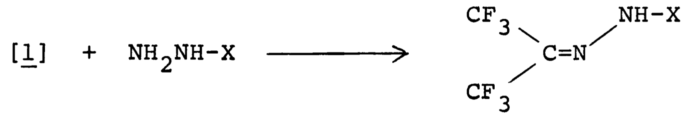


[1]    [2]

For example, a mixture of 1 (0.02 mole), p-toluidine (0.04 mole), and dimethylformamide (40 ml) was stirred at room temperature for 4 hours. During the reaction sulfur precipitated as a suspension. After removing sulfur by filtration, the reaction mixture was poured into water. The resulting oil was extracted with ethyl ether, and after drying with magnesium sulfate, the solvent was evaporated. Vacuum distillation of the residue afforded N-p-tolylhexafluoroisopropylidenimine [2, R= $C_6H_4$Me-p] (3.5 g, 69% yield from 1 in the above equation), bp 85-86°C/53 mmHg. The structure of this compound was confirmed by ir, $^1H$ and $^{19}F$ nmr, and mass spectra. Thus in the ir spectrum, a strong band at 1660 $cm^{-1}$ showed the presence of C=N, and in the $^{19}F$ nmr, two singlet peaks, -8.4 and -16.1 ppm from ext. $CF_3CO_2H$ in $CCl_4$, appeared which corresponded to syn- and anti-$CF_3$ respectively. In the mass spectrum, the parent peak, m/e 255, and other fragment peaks appeared appropriately.

Other arylamines, such as aniline, chloroanilines, and anisidines reacted similarly giving the corresponding N-arylimines. Alkylamines also gave N-alkylimines, but in poorer yields (Table 1). Methanol and ethanol, even at their boiling temperature, however, failed to react.

In addition to the N-aryl- and N-alkylimines mentioned above, the phenylhydrazone [3] and semicarbazone [4] of hexafluoroacetone have also been prepared directly from 1 and the corresponding carbonyl reagents.



[3] X = Ph

[4] X = $CONH_2$

Various nucleophiles, for example, alcohols and thiols reacted with N-arylimines [2], and the corresponding addition products, i.e., 2-alkoxy- and 2-alkylthio-2-arylaminohexafluoropropane were obtained. Details will be published in our later paper.

Table 1. Physical Properties of 2 - 4

| | R or X | Yield(%) | bp °C/mmHg (mp °C) | ir ($cm^{-1}$) (C=N) | $^{19}F$ nmr (δ ppm*) (syn-$CF_3$) | $^{19}F$ nmr (δ ppm*) (anti-$CF_3$) |
|---|---|---|---|---|---|---|
| 2 | Ph | 67 | 75/91 | 1680 | -8.6 | -16.2 |
| | o-Me$C_6H_4$ | 78 | 72-73/53 | 1698 | -8.4 | -15.0 |
| | m-Me$C_6H_4$ | 70 | 83-84/71 | 1604 | -8.4 | -16.4 |
| | m-Cl$C_6H_4$ | 78 | 71-72/21 | 1519 | -8.4 | -16.2 |
| | o-MeO$C_6H_4$ | 50 | 95-96/43 | 1666 | -9.2 | -12.7 |
| | n-Pr | 18 | 52-53/760 | 1691 | -7.4 | -13.6 |
| | n-Bu | 20 | 63-64/760 | 1634 | -7.2 | -14.7 |
| 3 | NHPh | 66 | 91-92/23 | 1664 | -8.7 | -15.8 |
| 4 | $NHCONH_2$ | 89.6 | (131-132) | 1640 | -11.3 | -12.9 |

* From ext. $CF_3CO_2H$ in $CCl_4$.

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