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REDUCTIVE DEFLUORINATION OF HEXAFLUOROACETONE ANIL

Yu. V. Zeifman

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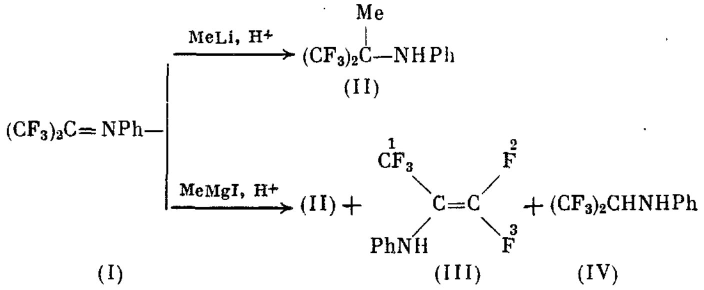
Hexafluoroacetone anil smoothly adds methyllithium at the C=N bond but undergoes reductive defluorination upon the action of Grignard reagents or metallic zinc to give 2-phenylaminopentafluoropropylene.

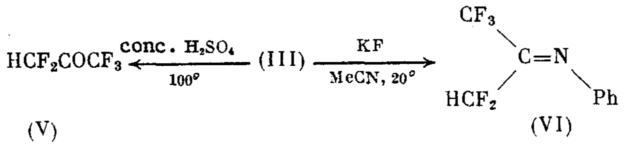
Imines of polyfluorinated carbonyl compounds participate in a broad range of nucleophilic reactions [1] but their conversions upon the action of organometallic reagents have not been studied extensively. $CF_3CH{=}NCOPh$ [2] and $CF_3C(CO_2Me){=}NR$ [3] give products of the addition of Grignard reagents or organocadmium compounds at the C=N bond in high yield.

We have established that the analogous reaction of hexafluoroacetone anil (I) with MeLi proceeds smoothly to give N-hexafluoro-tert-butylaniline (II). However, the reaction of anil (I) with MeMgI proceeds in a complicated manner [4] and leads to a ~1:1 mixture of amine (II) and 2-phenylaminopentafluoropropylene (III) along with a trace amount of hexafluoroisopropylaniline (IV) [5], which is a product of the reduction of anil (I).



The conversion of (I) to enamine (III) also occurs in the reactions of (I) with PhMgBr, $Me_2CHMgBr$, and Me_3CMgCl. In the latter two cases, enamine (III) and amine (IV) are formed in comparable amounts.

The structure of enamine (III) was demonstrated by acid hydrolysis to give pentafluoroacetone (V), isomerization to the anti isomer of anil (VI) by the action of alkali metal fluorides, and spectral methods.



Pentafluoroacetone anil (VI) was also obtained by an independent synthesis from ketone (V) and $Ph_3P{=}NPh$. NMR spectroscopy indicates that this reaction leads to the syn isomer of (VI). In the presence of fluoride anions, this isomer is converted to the anti isomer identical to that obtained from enamine (III) (the assignment of the isomers of (VI) to syn and anti forms was made by comparison with the data of Weigert [6]).

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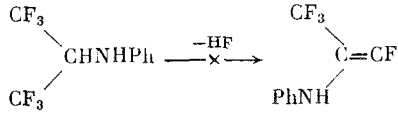
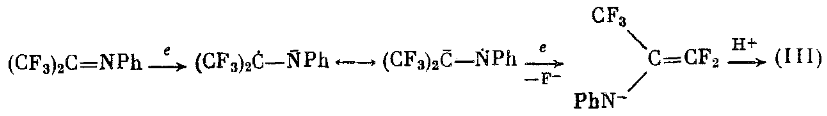
One of the possible pathways for the formation of enamine (III) in the reaction of anil (I) with Grignard reagents is the dehydrofluorination of amine (IV) by the action of RMgX. This hypothesis is in accord with the data of Kubota and Tanaka [7], who found that enamine (III) is formed in the reaction of amine (IV) with triethylamine in THF at reflux. However, we were unable to obtain enamine (III) by this method or by the action of MeMgI or a dehydroflorinating agent such as $Et_3N \cdot BF_3$ on amine (IV).

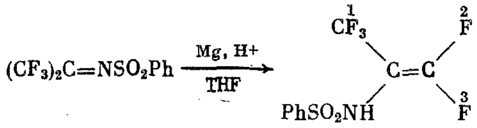


(IV) (III)

On the other hand, enamine (III) may be obtained in high yield in the reaction of anil (I) with zinc amalgam in DMF.* Thus, our data indicate that the formation of enamine (III) from anil (I) is a consequence of its reductive defluorination.† Either a metal or organometallic reagent may serve as the reducing agent [10].



The reductive defluorination of hexafluoroacetone imines is apparently a general reaction. Thus, aroylimines of hexafluoroacetone have been found to convert to the corresponding enamides by the action of $SnCl_2$ or metals [11]. In turn, we have found that benzosulfonylimine (VII) may undergo an analogous reaction.



(VII) (VIII)

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra were taken on a Perkin-Elmer R-32 spectrometer at 90 MHz for the ^1H NMR spectra and 84.6 MHz for the ^{19}F NMR spectra relative to TMS and CF_3CO_2H in CCl_4 as external standards. The IR spectra were taken on a UR-20 spectrometer.

N-Hexafluoro-tert-butylaniline (II). A sample of 0.5 g MeLi (from MeBr and lithium) in 15 ml ether was added to 5.4 g anil (I) in 15 ml abs. ether at 0-5°C. The mixture was warmed to 20°C and, after 3 h, poured into a solution obtained by mixing one part concentrated hydrochloric acid and five parts water. The organic layer was dried and distilled to give 3.8 g (72%) amine (II), bp 58-60°C (10 mm), n_D^{20} 1.4242. Found: C, 47.02; H, 3.82; F, 43.92%. Calculated for $C_{10}H_9F_6N$: C, 46.77; H, 3.76; F, 43.86%. PMR spectrum (δ, ppm): 1.3 s (Me), 3.5 s (NH), 6.8 m (Ph). ^{19}F NMR spectrum (δ, ppm): -0.7 s (CF_3).

2-Phenylaminopentafluoropropylene (III). A sample of 1 g $HgCl_2$ was added with stirring to 8 g zinc powder in 50 ml abs. DMF. At the end of the exothermal reaction, 17.9 g anil (I) was added dropwise, maintaining the temperature of the mixture below 30°C. After 4 h, the reaction mixture was poured into a solution obtained by mixing one part concentrated hydrochloric acid and five parts water. The oily precipitate was extracted with ether, dried over $MgSO_4$, and distilled to give 13.6 g (83%) enamine (III), bp 76-79°C (20 mm), n_D^{20} 1.4538 [7]. IR spectrum (ν_{max}, cm^{-1}): 1730, 1760, 3420. PMR spectrum (δ, ppm): 4.0 br.s (NH), 6.6 m (Ph). ^{19}F NMR spectrum (δ, ppm): -12 d.d (F^1), 2.4 d.q (F^3), 4.6 d.q (F^2), $J_{F^1-F^2} = 21.6$, $J_{F^1-F^3} = J_{F^2-F^3} = 9.6$ Hz. Enamine (III) was unchanged after prolonged storage below 0°C but tar formation gradually occurred at 20°C.

A mixture of 4.4 g enamine (III) and 8 ml concentrated sulfuric acid was heated for 45 min at 100°C. A total of 1.7 g (60%) ketone (V) was distilled off, which was identical to an authentic sample as indicated by NMR spectroscopy and gas-liquid chromatography [12].

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*These results were presented in our preliminary communication [8].

†Shchepin et al. [9] have presented information on the reductive dechlorination of chloral imines by zinc.

A mixture of 2 g KF, 4.3 g enamine (III), and 20 ml abs. acetonitrile was stirred for 3 h and poured into a solution obtained by mixing one part concentrated hydrochloric acid and five parts water. The oily precipitate was extracted with ether, dried, and distilled at 5 mm Hg to give 3.9 g of a mixture consisting of 38% enamine (III), 46% anti-isomer (VI), and 16% amine (IV) as indicated by ^{19}F NMR spectroscopy. ^{19}F NMR spectrum of anti-(VI) (δ, ppm): 4.9 t (CF_3), 5.0 d.t (CF_2), J_{F-F} = 7.5, J_{F-H} = 54.5 Hz.

Reaction of Hexafluoroacetone Anil with Grignard Reagents. A sample of 4.5 g anil (I) in 10 ml ether was added dropwise to MeMgI (obtained from 3.5 g MeI and 0.6 g Mg) in 20 ml ether with ice cooling. After 6 h, the mixture was hydrolyzed with a solution obtained by mixing one part concentrated hydrochloric acid and five parts water. The ethereal solution was distilled to give 3.7 g of a fraction with bp 72-78°C (12 mm) containing 54% amine (II), 43% enamine (III), and 3% amine (IV) as indicated by ^{19}F NMR spectroscopy. Analogously, 4.5 g anil (I) and 3.2 g $Me_2CHMgBr$ gave 3 g of a mixture containing 60% enamine (III) and 40% amine (IV).

Pentafluoroacetone Anil (VI). A sample of 4.5 g pentafluoroacetone was added gradually to a suspension of 10 g triphenylphosphinophenylimine in 25 ml abs. ether. At the end of the exothermal reaction, the precipitate was filtered off. Distillation of the filtrate gave 5.1 g (75%) syn isomer anil (VI), bp 68-70°C (20 mm), n_D^{20} 1.4390 [13]. ^{19}F NMR spectrum (δ, ppm): −8.6 t (CF_3), 42.9 d.t (CF_2), J_{F-F} = 7.5, J_{F-H} = 52.5 Hz. A mixture of 0.5 g KF, 0.8 g syn-(VI), and 4 ml acetonitrile was stirred for 3 h at 20°C. Ordinary work-up gave anti-(VI).

2-Phenylsulfonylaminopentafluoropropylene (VIII). A sample of 0.6 g $HgCl_2$ was added with stirring to 0.7 g magnesium in 25 ml abs. THF and then sulfonylimine (VII) in 10 ml THF was added, maintaining the temperature below 20°C. After 2 h, the reaction mixture was poured into a solution obtained by mixing one part concentrated hydrochloric acid and five parts water and extracted with ether. The ethereal layer was dried and evaporated. The solid residue was recrystallized from CCl_4 to give 3.2 g (49%) sulfamide (VIII), mp 82-86°C. Found: C, 37.79; H, 2.13; F, 32.87%. Calculated for $C_9H_6F_5NO_2S$: C, 37.63; H, 2.09; F, 33.10%. IR spectrum (ν_{max}, cm^{-1}): 1750, 3250. ^{19}F NMR spectrum in THF (δ, ppm): −14.2 d.d (F^1), −2.4 q (F^3), 0.7 q (F^2), $J_{F^1-F^2}$ = 20, $J_{F^1-F^3}$ = 10 Hz.

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