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A Novel Route to *N*-Phenyl-*C*-(trifluoromethyl)nitrilimine from 3-Phenyl-5-trifluoromethyl-2,3-dihydro-1,3,4,2-oxadiazaphosphole

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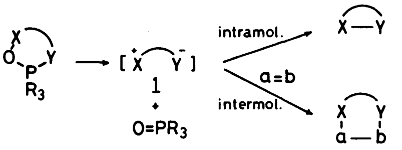
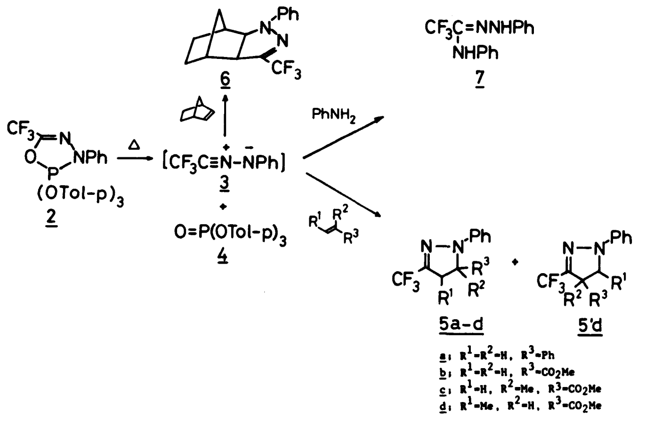
Synopsis. Thermolysis of 3-phenyl-5-trifluoromethyl-2,2,2-tris-(*p*-tolyloxy)-2,3-dihydro-1,3,4,2-oxadiazaphosphole in the presence of various olefins gave the 1,3-dipolar cycloadducts of *N*-phenyl-*C*-(trifluoromethyl)nitrilimine *in situ* formed. The similar decomposition in aniline afforded *N*-phenyltrifluoroacetamide phenylhydrazone.

Pentacovalent phosphorus compounds (phosphoranes) have high potential as synthetic reagents[1] but only a little information is available.[2] A cyclic oxyphosphorane is known to decompose with the formation of phosphine oxide and a polar intermediate (**1**) which cyclizes inter- or intramolecularly as shown below. Such a reaction mode could be utilized as a general method for the synthesis of heterocyclic compounds:[3] for example, Burger and his co-workers have been exploring the reactions of benzonitrile bis(trifluoromethyl)ylide generated from 5,5,5-trialkoxy-2-phenyl-4,4-bis(trifluoromethyl)-4,5-dihydro-1,3,5-oxazaphosphole.[4] We have previously described the preparation of 3-phenyl-5-trifluoromethyl-2,2,2-tris(*p*-tolyloxy)-2,3-dihydro-1,3,4,2-oxadiazaphosphole (**2**) and its possibile use as a precursor of *N*-phenyl-*C*-(trifluoromethyl)nitrilimine (**3**).[5]



In the present paper, we wish to report that thermolysis of the phosphole **2** in the presence of various olefins or nucleophiles like aniline affords the corresponding 1,3-dipolar cycloadducts or 1,3-adducts, respectively, of the nitrilimine **3** formed *in situ*. Such results must indicate the phosphole **2** to be the novel effective source of the nitrilimine **3**.[6]

The thermal decomposition of **2** in the presence of excess styrene was carried out at 140 °C for 24 h to give 1,5-diphenyl-3-trifluoromethyl-2-pyrazoline (**5a**) in 73% yield along with 65% of tris(*p*-tolyl) phosphate (**4**). A similar cleavage did not take place at 110 °C, the greater part of **2** being recovered unchanged. In the presence of methyl acrylate and methacrylate, thermolysis of **2** provided the corresponding pyrazolines **5b** and **5c** in 98 and 73% yields, respectively. On the other hand, in the case of methyl crotonate, the formation of both the pyrazoline **5d** and its regioisomer **5′d** in the ratio of 80/20 was found. The structure of these pyrazolines was determined by their elemental analyses and spectral data or by comparison with our authentic samples. The regioselectivity of these cycloadditions of **3** derived from **2** was analogous to that from *N*-phenyltrifluoroacetohydrazonoyl chloride which, for example, with methyl crotonate, gives a 90/10 mixture of **5d** and **5′d**.[7]



Cycloaddition was also found to occur when **2** was decomposed in the strained olefin like norbornene, where *the syn-adduct* **6** *was exclusively obtained in* 48% yield. The exo-configuration of **6** is supported by the absence of coupling between the bridgehead protons and the corresponding vicinal pyrazoline protons in ^{1}H NMR.[8] Similarly, on the cleavage of **2** in aniline, the 1,3-addition product, *N*-phenyltrifluoroacetamide phenylhydrazone (**7**), was produced in 61% yield.

The present alternative route to **3** has the advantage that the thermal decomposition of **2** is carried out at a relatively low temperature and under neutral conditions.[9]

Experimental

All melting and boiling points are uncorrected. The IR spectra were recorded on a JASCO IRA-1 spectrometer. The ^{1}H and ^{31}P NMR spectra were measured with JEOL JNM-PMX 60 and FX 90Q spectrometers using tetramethylsilane and 85% phosphoric acid as internal and external standards, respectively; the chemical shifts are given in δppm downfield. The MS spectra were obtained with a Finnigan 4023 GC-MS DS spectrometer.

Preparation of **2**. Phosphorus pentachloride 5.20 g (24.9 mmol) was added to a stirred suspension of 4.74 g (23.2 mmol) of *N*-phenyltrifluoroacetohydrazide in 40 ml of toluene. The mixture was stirred at room temperature for an additional 2 h with evolution of hydrogen chloride. The solvent was evaporated under reduced pressure to leave oily matter which was distilled to give 7.33 g (93%) of 2,2,2-trichloro-3-phenyl-5-trifluoromethyl-2,3-dihydro-1,3,4,2-oxadiazaphosphole, bp 124—126 °C/12 mmHg (1 mmHg=133.322Pa), IR(film) 1650 cm^{-1} (C=N), ^{1}H NMR (CDCl$_3$) δ=7.3 (br. s). A mixture of 2.00 g (5.9 mmol) of trichlorophosphole thus obtained and 3.19 g (17.7 mmol) of *O*-trimethylsilyl-*p*-cresol in 20 ml of toluene was refluxed for 4.5 h. The solvent was removed to leave a residue which was recrystallized from hexane to give the colorless crystals **2**, 1.78 g (54%), mp 96—97 °C, IR (KBr) 1648 cm^{-1} (C=N),

^{1}H NMR (CCl_4) δ=2.3 (s, 9H), 6.8 (A_2X_2, 12H), and 7.4 (br. s, 5H), ^{31}P NMR ($CDCl_3$) δ=−69.0, MS (CI, m/z) 583 (M+C_2H_5)$^+$ and 555 (M+H)$^+$.

Found: C, 62.82; H, 4.62; N, 4.78. Calcd for $C_{29}H_{26}F_3N_2O_4P$: C, 62.82; H, 4.73; N, 5.05.

Thermolysis of **2** *in Styrene.* A mixture of 0.55 g (1.0 mmol) of **2** and 0.52 g (5.0 mmol) of styrene in 20 ml of xylene was refluxed for 24 h and the solvent was removed. The resulting oily matter was placed on a column (silica gel) and eluted with hexane–chloroform (1:1) to give 0.21 g (72%) of **5a** and 0.24 g (65%) of **4**. The pyrazoline **5a** was further purified by recrystallization from hexane. **5a**; mp 87.5—88.5 °C, IR (KBr) 1610 cm^{-1} (C=N), ^{1}H NMR (CCl_4) δ=2.88 (ddq, J=8, 18, 2 Hz, 1H), 3.60 (ddq, J=12, 18, 2 Hz, 1H), 5.25 (dd, J=8, 12 Hz, 1H), and 6.5—7.5 (m, 10H).

Found: C, 66.25; H, 4.52; N, 9.75. Calcd for $C_{16}H_{13}F_3N_2$: C, 66.20; H, 4.51; N, 9.65.

In a similar manner, **6** was isolated in 47% yield. **6**; mp 78.5—79.5 °C (recrystallized from methanol), IR (KBr) 1595 cm^{-1} (C=N and Ph), ^{1}H NMR ($CDCl_3$) δ=1.1—1.7 (m, 6H), 2.5—2.8 (m, 2H), 3.33 (dm, J=10 Hz, 1H), 4.20 (d, J=10 Hz, 1H), and 6.8—7.4 (m, 5H).

Found: C, 64.44; H, 5.34; N, 10.03. Calcd for $C_{15}H_{15}F_3N_2$: C, 64.28; H, 5.39; N, 9.99.

Thermolysis of 2 in Methyl Crotonate. A mixture of 1.50 g (2.7 mmol) of 2 and 3.0 ml of methyl crotonate in a sealed tube was stirred at 140—145 °C for 24 h. The product ratio was determined by GLC analysis of the reaction mixture; **5d**/**5′d** ratio of 80/20. After excess methyl crotonate was removed, 0.73 g (94%) of a mixture of **5d** and **5′d** was obtained by column chromatography (silica gel, hexane–chloroform, 3:2). Each pyrazoline was isolated by preparative GLC. **5d**; IR (film) 1750 cm^{-1} (C=O), ^{1}H NMR (CCl_4) δ=1.43 (d, J=7 Hz, 3H), 3.51 (dqm, J=7, 7 Hz, 1H), 3.70 (s, 3H), 4.35 (d, J=7 Hz, 1H), and 6.7—7.4 (m, 5H). **5′d**; IR (film) 1750 cm^{-1} (C=O), ^{1}H NMR (CCl_4) δ=1.37 (d, J=7 Hz, 3H), 3.63 (dm, 1H), 3.72 (s, 3H), 4.77 (dq, J=7, 7 Hz, 1H), and 6.6—7.3 (m, 5H).

Found: C, 54.43; H, 4.57; N, 9.75 (for a mixture of **5d** and **5′d**). Calcd for $C_{13}H_{13}F_3N_2O_2$: C, 54.55; H, 4.58; N, 9.79.

Similarly, **5b** and **5c** were isolated in 98 and 73% yields, respectively. **5b**; mp 58—60 °C (lit,[7] 60—61.5 °C), IR (KBr) 1745 (C=O) and 1620 cm^{-1} (C=N), ^{1}H NMR ($CDCl_3$) δ=2.8—3.5 (m, 2H), 3.71 (s, 3H), 4.87 (dd, J=11, 9 Hz, 1H), and 6.8—7.4 (m, 5H). **5c**; colorless oil, IR (film) 1745 cm^{-1} (C=O), ^{1}H NMR (CCl_4) δ=1.59 (s, 3H), 3.00 (dm, J=17 Hz 1H), 3.53 (dm, J=17 Hz, 1H), 3.73 (s, 3H), and 6.7—7.4 (m, 5H).

Found: C, 54.40; H, 4.57; N, 9.73. Calcd for $C_{13}H_{13}F_3N_2O_2$: C, 54.55; H, 4.58; N, 9.79.

Thermolysis of **2** *in Aniline.* A mixture of 1.50 g (2.7 mmol) of **2** and 5.04 g (54.2 mmol) of aniline in 30 ml of xylene was refluxed for 15 h and the solvent was removed. To the residual oil was added diethyl ether and the mixture was washed twice with water, dried over magnesium sulfate, and evaporated. The resulting oily matter was submitted to column chromatography (silica gel, hexane–chloroform, 1:1) to give 0.46 g (61%) of **7** which was further purified by recrystallization. **7**; mp 66.5—67.5 °C (hexane), IR (KBr) 3360 cm^{-1} (NH), ^{1}H NMR ($CDCl_3$) δ=5.5 (br. s, 1H) and 6.8—7.4 (m, 11H).

Found: C, 60.07: H, 4.28; N, 15.10. Calcd for $C_{14}H_{12}F_3N_3$: C, 60.21; H, 4.33; N, 15.05.

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