

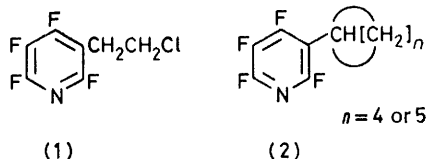
## Heterocyclic Polyfluoro-compounds. Part 32.<sup>1a</sup> Photochemical Reactions of 3-Chlorotetrafluoro- and 3,5-Dichlorotrifluoro-pyridines with Olefins, and their Photoreduction<sup>1b</sup>

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Ethylene reacts photochemically with 3-chlorotetrafluoropyridine to yield 3-(2-chloroethyl)tetrafluoropyridine, and cyclo-pentene and -hexene yield the corresponding 3-cycloalkyltetrafluoropyridines. Photochemical reaction of cyclohexene with 3,5-dichlorotrifluoropyridine yields 3-chloro-5-cyclohexyltrifluoropyridine. The chlorine in 3-chlorotetrafluoropyridine, and one of the chlorines in 3,5-dichlorotrifluoropyridine, is readily reduced photochemically in solvents such as ethanol, diethyl ether, or acetone.

WHEREAS 4-substituted tetrafluoropyridines are readily available by nucleophilic attack upon pentafluoropyridine,<sup>2</sup> 2-substituted tetrafluoropyridines are available only by co-pyrolysis of perfluorocyclohexa-1,3-diene with cyanides,<sup>3</sup> from 2,3,4,5-tetrafluoropyridine-6-carbonitrile,<sup>4</sup> or indirectly from phenyl 2,3,5,6-tetrafluoropyridyl sulphone.<sup>4</sup> 3-Chlorotetrafluoropyridine<sup>5</sup> provides potential access to a variety of 3-substituted tetrafluoropyridines,<sup>6</sup> but this has been little exemplified. Some photochemical reactions of 3-chlorotetrafluoropyridine, and of the related 3,5-dichlorotrifluoropyridine, are now described which offer promise as a route to a variety of 3-substituted fluoropyridines.

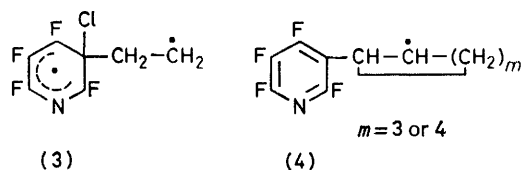
Irradiation with u.v. light of a solution of ethylene in 3-chlorotetrafluoropyridine slowly yields 3-(2-chloroethyl)tetrafluoropyridine (1) in good yield (77%) in a reaction which formally involves insertion of ethylene into the C-Cl bond. In contrast, similar reactions with cyclo-pentene and -hexene give good yields of the cyclo-



alkylpyridines (2), contaminated with small amounts of what appear to be cycloalkenyltetrafluoropyridines. Analogously, cyclohexene and 3,5-dichlorotrifluoropyridine yield 3-chloro-5-cyclohexyltrifluoropyridine (87%). A chlorine atom of the parent chlorofluoropyridines may readily be replaced photochemically by hydrogen. Irradiation of solutions of 3-chlorotetrafluoropyridine in ethanol, diethyl ether, or acetone gives 2,3,4,6-tetrafluoropyridine, previously available by catalytic reduction,<sup>7</sup> and irradiation of a solution of 3,5-dichlorotrifluoropyridine in diethyl ether results in replacement of one chlorine by hydrogen, a reaction which may be of synthetic value since catalytic reduction is difficult to control at this stage.

It is tempting to ascribe the formation of the ethylene insertion product (1) to intramolecular chlorine atom transfer in an intermediate diradical (3). If a similar

intermediate diradical is involved in the cycloalkene reactions, chlorine atom elimination to give a radical (4) which abstracts an allylic hydrogen atom from the cycloalkene, the resulting cycloalkenyl radical then



dimerising, appears to be the preferred reaction. Tetrafluoropyridyl radicals are presumed to be involved in the photoreduction of 3-chlorotetrafluoropyridine, but they cannot account for the products of reactions with olefins for the following reasons. Addition to ethylene would give a 2-(tetrafluoropyridyl)ethyl radical, which would disproportionate or dimerise, or react further with ethylene, rather than abstract a chlorine atom. With the cycloalkenes, hydrogen abstraction rather than addition to the double bond might well occur, yet tetrafluoropyridine was not detected. Here, however, the ejection of a chlorine atom from the intermediate diradical is preferred, rather than rearrangement. The 2-tetrafluoropyridylcycloalkyl radical so produced can then give rise to the observed products largely by hydrogen abstraction from the cycloalkene, and by disproportionation.

An intermediate analogous to (3) may well be involved in the photochemical addition of olefins to pentafluoropyridine, but fluorine atom transfer does not occur, and cyclisation results instead.<sup>7</sup> The photoreductions are analogous to those observed for pentachloropyridine, where the 3-chlorine is replaced by hydrogen,<sup>8</sup> and for chlorobenzene.<sup>9</sup>

### EXPERIMENTAL

Experimental techniques were similar to those used earlier.<sup>1</sup>

*Photochemical Reactions of 3-Chlorotetrafluoropyridine.*—  
(a) *With ethylene.* 3-Chlorotetrafluoropyridine<sup>5</sup> (4.61 g, 24.8 mmol) and ethylene (2.46 g, 87.9 mmol), sealed *in vacuo* in a silica ampoule (*ca.* 300 cm<sup>3</sup>) and the liquid phase irradiated for 176 h with u.v. light from an Hanovia UVS 500 medium-

pressure mercury lamp at a distance of 30 cm, gave a volatile fraction comprising unchanged ethylene (2.27 g, 81.1 mmol, 92% recovery) and chlorotetrafluoropyridine (3.96 g, 21.3 mmol, 86%), and a residue (0.8 g). This was distilled at 140 °C/1 mmHg and purified by g.l.c. (4 m Apiezon L on Celite at 150 °C) to give 3-(2-chloroethyl)-tetrafluoropyridine (0.58 g, 2.7 mmol, 77% yield based upon the pyridine converted) (Found: C, 39.6; H, 1.8; Cl, 17.0; F, 35.9; N, 6.6.  $C_7H_4ClF_4N$  requires C, 39.3; H, 1.9; Cl, 16.6; F, 35.6; N, 6.6%) as a colourless liquid;  $\delta_F^*$  (neat liquid) 3.7 (F-2), -10.5 (F-6), -40.6 (F-4), and -90.9 p.p.m. (F-5);  $\tau$ -values 6.36 and 6.95 (typical  $XCH_2CH_2Y$  pattern);  $m/e$  213 ( $M^+$ , 31.2%), 177 ( $M - HCl$ , 4.3), and 164 ( $M - CH_2Cl$ , 100).

(b) *With cyclopentene.* 3-Chlorotetrafluoropyridine (2.60 g, 14.0 mmol) and cyclopentene (3.29 g, 48.4 mmol), sealed *in vacuo* in a silica ampoule (ca. 30 cm<sup>3</sup>) and the liquid phase irradiated for 128 h, gave unchanged cyclopentene (2.43 g, 35.7 mmol, 74% recovery), the pyridine (1.73 g, 9.3 mmol, 66% recovery), and a fraction, b.r. 53–60 °C/10 mmHg (1.2 g), which was separated by g.l.c. (4 m Apiezon L at 125 °C) to give 3-cyclopentyltetrafluoropyridine (0.83 g, 3.8 mmol, 81% yield based upon chlorotetrafluoropyridine consumed) (Found: C, 55.1; H, 3.8; F, 34.4; N, 6.1.  $C_{10}H_9F_4N$  requires C, 54.8; H, 4.1; N, 6.4; F, 34.7%) as a colourless liquid [m.p. 16–18 °C (sealed tube)];  $\delta_F^*$  6.3 (F-2), -12.6 (F-6), -41.3 (F-4), and -92.6 p.p.m. (F-5);  $\tau$ -values 7.0 (CH) and 8.1–8.7 ( $CH_2$ );  $m/e$  219 ( $M^+$ , 17.5%) and 177 ( $C_7H_3NF_4$ , 100), and a component tentatively identified as 3,3'-bicyclopentenyl (0.31 g, 2.3 mmol, 10% yield based upon cyclopentene taken) by i.r. spectroscopy. The <sup>1</sup>H n.m.r. spectrum of the cyclopentylpyridine under high gain (weak absorptions at ca.  $\tau$  4.5) and the mass spectrum ( $m/e$  217) indicated that it contained small amounts of a cyclopentenyltetrafluoropyridine.

(c) *With cyclohexene.* 3-Chlorotetrafluoropyridine (6.42 g, 34.5 mmol) and cyclohexene (7.24 g, 88.3 mmol), sealed in a silica ampoule (ca. 30 cm<sup>3</sup>) and the liquid phase irradiated for 112 h, gave unchanged cyclohexene (4.82 g, 58.8 mmol, 67% recovery) and the chloropyridine (4.55 g, 24.5 mmol, 71% recovery), and a residue which was distilled at 65–72 °C/10 mmHg to give a fraction (3.8 g), which was separated by g.l.c. (4 m Apiezon L at 140 °C) to give 3-cyclohexyltetrafluoropyridine (2.10 g, 9.0 mmol, 90% yield based upon the pyridine consumed) (Found: C, 56.6; H, 4.7; F, 32.6; N, 5.8.  $C_{11}H_{11}F_4N$  requires C, 56.5; H, 4.7; F, 32.6; N, 6.0%), as white crystals, m.p. 24–26 °C (sealed tube);  $\delta_F^*$  6.4 (F-2), -12.3 (F-6), -41.2 (F-4), and -91.4 p.p.m. (F-5);  $\tau$ -values 7.3 (CH) and 8.1–9.2 (5  $CH_2$ ); and  $m/e$  233 ( $M^+$ , 27.7%) and 177 ( $C_7H_3NF_4$ , 100%), and 3,3'-bicyclohexenyl (1.62 g, 10.0 mmol, 23% based upon cyclohexene taken), identical (i.r., n.m.r., and mass spectra) with a sample prepared by the reaction of 3-bromocyclohexene with magnesium.<sup>10</sup> The <sup>1</sup>H n.m.r. spectrum and the mass spectrum ( $m/e$  231) indicated that the cyclohexylpyridine contained small amounts of a cyclohexenyltetrafluoropyridine.

(d) *With diethyl ether.* 3-Chlorotetrafluoropyridine (3.31 g, 17.8 mmol) and diethyl ether (11.7 g, 158.1 mmol), sealed in a silica ampoule (ca. 30 cm<sup>3</sup>) and irradiated for 122 h, gave, after removal of unchanged ether by distillation, a mixture, which was separated by g.l.c. (4 m Apiezon L at 100 °C) to give 2,3,4,6-tetrafluoropyridine (0.56 g, 3.7 mmol, 81%

\* Positive values are to low-field of external trifluoroacetic acid.

based upon the chloropyridine used), b.p. 115 °C (lit.,<sup>6</sup> 115–116 °C), spectroscopically (i.r. and n.m.r.) identical with a known sample, unchanged chlorotetrafluoropyridine (2.51 g, 13.5 mmol, 76% recovery), and 2,3-diethoxybutane (0.60 g, 4.1 mmol, 5% yield based upon diethyl ether taken, which was identified by i.r. and n.m.r. spectroscopy:  $\tau$ -values 6.65 (CHO), 6.73 ( $CH_2O$ ), 9.01 ( $CH_3CH_2$ ), and 9.04 and 9.11 ( $CH_2-CH$ ), as a mixture of  $\pm$ - and *meso*-isomers.

(e) *Reductions.* Solutions (0.4 M) of 3-chlorotetrafluoropyridine in ethanol, diethyl ether, acetone, or cyclohexane were irradiated for 142 h in Pyrex or silica ampoules. Little or no reduction occurred in Pyrex (by g.l.c.), and in silica the percentage reduction to tetrafluoropyridine was 66, 43, 25, and <5% for solutions in ethanol, diethyl ether (for comparison), acetone, and cyclohexane, respectively. The reaction in cyclohexane gave small amounts of 3-cyclohexyltetrafluoropyridine [identified by g.l.c., see (c) above], together with traces of several other components.

*Reactions of 3,5-Dichlorotrifluoropyridine.*—(a) *With cyclohexene.* 3,5-Dichlorotrifluoropyridine (7.32 g, 36.2 mmol) and cyclohexene (9.56 g, 116.6 mmol), sealed in a silica ampoule (ca. 50 cm<sup>3</sup>) and irradiated for 85 h, gave unchanged cyclohexene (7.96 g, 97.1 mmol, 83% recovery) and the dichlorotrifluoropyridine (5.91 g, 29.3 mmol, 81% recovery), and a residue. This was distilled at 100 °C/1 mmHg and separated by g.l.c. (4 m Apiezon L at 160 °C) to give 3,3'-bicyclohexenyl (0.97 g, 6.0 mmol, 10% yield based upon cyclohexene taken) and 3-chloro-5-cyclohexyltrifluoropyridine (1.50 g, 6.0 mmol, 87% based upon the dichloropyridine consumed) (Found: C, 53.0; H, 4.5; Cl, 14.2; F, 22.7; N, 5.4.  $C_{11}H_{11}ClF_3N$  requires C, 52.9; H, 4.4; Cl, 14.2; F, 22.8; N, 5.6%), as colourless crystals, m.p. 51–53 °C (sealed tube);  $\delta_F^*$  9.1 (F-6), 4.9 (F-2), and -20.2 p.p.m. (F-4);  $\tau$ -values 7.0 (CH) and 7.6–8.3 (5  $CH_2$ ); and  $m/e$  249 ( $M^+$ , 42.5%) and 193 ( $C_7H_3NF_3^{35}Cl$ , 100). The <sup>1</sup>H n.m.r. and mass spectrum ( $m/e$  247) indicated the presence of small amounts of chlorocyclohexenyltrifluoropyridine.

(b) *With diethyl ether.* 3,5-Dichlorotrifluoropyridine (5.20 g, 25.7 mmol) and diethyl ether (17.16 g, 231.9 mmol), sealed in a silica ampoule (100 cm<sup>3</sup>) and the liquid phase irradiated for 91 h, gave, after removal of the ether by distillation, a mixture which was separated by g.l.c. (4 m Apiezon L at 105 °C) to give 3-chloro-2,4,6-trifluoropyridine (1.17 g, 7.0 mmol, 85% yield based upon dichlorotrifluoropyridine consumed) (Found: C, 36.1; H, 0.5; Cl, 21.0; F, 34.0; N, 8.3%;  $M^+$ , 167. Calc. for  $C_5HClF_3N$ : C, 35.8; H, 0.6; Cl, 21.2; F, 34.0; N, 8.4%;  $M$ , 167), b.p. 130 °C (lit.,<sup>11</sup> 128–129 °C), identified by n.m.r. spectroscopy, 2,3-diethoxybutane (1.21 g, 8.3 mmol, 7% yield based upon diethyl ether taken), and unchanged 3,5-dichlorotrifluoropyridine (3.53 g, 17.5 mmol, 68% recovery).

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