ed with hexane. The organic extracts were washed with sodium bicarbonate solution and the solvent was removed under reduced pressure, affording 20.5 g of recovered olefin **2**.

**Acknowledgment.** The author wishes to thank Mr. C. Dmochowski and Mrs. A. Cerasia for their able technical assistance during the course of the above investigation.

**Registry No.**—**2**, 32540-36-6; **3**, 54689-00-8; **4**, 54713-02-9; **7**, 54689-01-9; **8**, 54713-03-0; **9**, 54689-02-0; **11**, 54724-65-1; **12**, 54689-03-1; **13**, 54713-04-1; **14**, 54689-04-2; **15**, 54689-05-3; **16**, 54689-06-4; peracetic acid, 79-21-0; potassium permanganate, 7722-64-7; sodium dichromate, 10588-01-9; diborane, 19287-45-7; *m*-chloroperbenzoic acid, 937-14-4.

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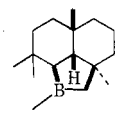


i

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# Addition of Aryl Nitrenes to Olefins[1]

Rudolph A. Abramovitch,* Stanley R. Challand, and Yorinobu Yamada

*Department of Chemistry, University of Alabama, University, Alabama 35486*

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Pentafluoronitrosobenzene undergoes an "ene"-type reaction with a variety of olefins. When triethyl phosphite is added to the olefin *before* the addition of the nitroso compound (inverse addition), pentafluorophenylnitrene is formed which adds stereospecifically to a number of olefins to give the corresponding aziridines. The possibility of a 1,3-dipolar addition of the nitrene precursor followed by elimination of triethyl phosphate has been discounted. Pentafluorophenylnitrene, generated photochemically from the azide, behaves analogously, but thermal decomposition of the azide in the presence of olefins gives products arising from an initial 1,3-dipolar adduct. 4-Azidotetrachloropyridine behaves similarly but the derived nitrene is less electrophilic.

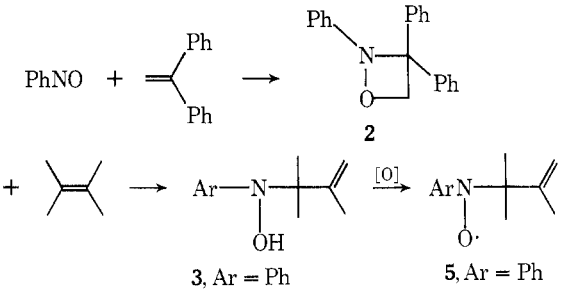
Authenticated examples of the addition of thermally generated discrete nitrenes to olefinic bonds to give aziridines have appeared infrequently in the literature, since azides, the usual nitrene precursors, themselves react with aliphatic multiple bonds at temperatures generally lower than those required to generate the corresponding free nitrene.[2] The issue is further complicated by the fact that the 1,2,3-triazolines thus produced may subsequently lose nitrogen to give the same aziridines as would be expected from nitrene addition.[3]

The addition of ethoxycarbonylnitrene, generated by photolysis of ethyl azidoformate at ambient temperature, to olefins to give *N*-carbethoxyaziridines has been studied extensively.[4] It was shown that both singlet and triplet nitrene added to the olefin but that only the singlet species added stereospecifically.[5] Addition of triplet nitrene occurred via a 1,3-diradical intermediate which resulted in stereochemical scrambling. Addition to conjugated dienes is usually in the 1,2 manner,[5] rather than 1,4 manner,[6] except in certain cases such as the additions to pyrroles or to thiophenes, e.g., the additions of *N*-carbethoxynitrene to pyrroles or to thiophenes,[7a] or those which proceed via a triplet diradical, e.g., the addition of cyanonitrene to cyclooctatetraene.[7b]

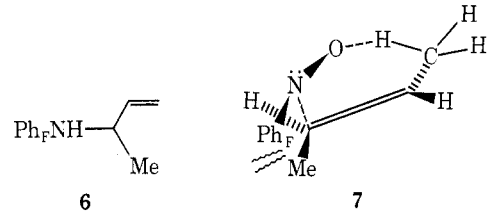
Evidence for the direct addition of aryl nitrenes to olefins is scanty, there being only one clear-cut example, that of aziridine formation during the photolysis of ferrocenyl azide in cyclohexene.[8] Formation of 1,2,3-triazolines in the thermal reaction of aryl azides with olefins or acetylenes is well known,[3,9] as is the reaction with certain other unsaturated species, such as enol ethers[10] and enamines.[11] With highly polarized double bonds such as these, the addition is usually regiospecific.

We have previously shown that pentafluorophenylni-

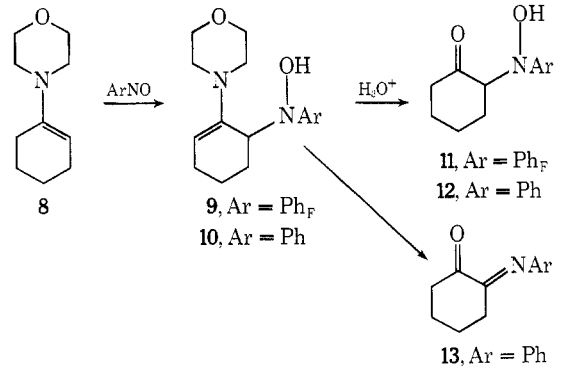
trene, generated by triethyl phosphite deoxygenation of pentafluoronitrosobenzene (**1**, Ar = $C_6F_5$), undergoes addition to aromatic bonds under conditions under which other less electrophilic aryl nitrenes do not.[12] Furthermore, since the procedure does not use an azide as the starting material, it offered promise as a means of investigating the behavior of an aryl nitrene toward olefins. A number of reports have, however, appeared in the literature exemplifying the reactivity of aryl nitroso compounds toward olefins. Varying types of reactivity are found. For instance, nitrosobenzene adds to 1,1-diphenylethylene in a [2 + 2] manner to give oxazetidine (**2**),[13] whereas with styrene a mixture of nitrones is obtained.[14] When the olefin possesses allylic hydrogens an "ene"-type reaction is favored; for example, tetramethylethylene gives the hydroxylamine **3**, which undergoes rapid aerial oxidation to the nitroxide **5**[15] (which




we had independently confirmed). In view of these facts, the reactivity of **1** toward our projected olefinic substrates was investigated. An immediate reaction with tetramethylethylene took place, giving hydroxylamine **4a** in quantitative yield. *p*-Nitrosobenzotrifluoride behaved similarly. Unlike **3**, **4a** showed no tendency toward aerial oxidation. A similar reaction was observed between **1** and *cis*-2-butene, but with *trans*-2-butene under similar conditions a complex mixture of products was obtained in which amine **6** was apparent. This difference in behavior suggests that steric effects might be important in the highly ordered transition state in keeping with a concerted "ene"-type mechanism, **7**. Styrene, cyclohexene, 1-methylcyclohexene, and

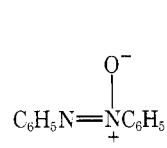



1,2-dimethylcyclohexene also gave complex mixtures in which the amines analogous to **6** were detected (cf. ref 15c), but the enamine **8** gave a hydroxylamine (**9**) analogous to **3**

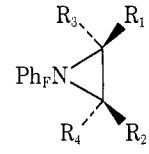



and **4**. A similar reaction with nitrosobenzene has been reported[16] to give **10** which could be hydrolyzed to **12** by brief treatment with dilute aqueous acid, and to **13** by longer treatment (15 hr). Only hydroxylamine **11** was obtained from **9**, however, even after prolonged acid treatment. No appreciable reaction took place between **1** and stilbenes, or *n*-butyl vinyl ether.

For the projected nitrene additions, the problem of reaction of the precursor with substrate was overcome by employing inverse addition. Thus, when **1** was added to a solution of triethyl phosphite in excess tetramethylethylene, decafluoroazoxybenzene (**14**), hydroxylamine **4**, and the expected aziridine, **15**, were formed in 14, 5.5, and



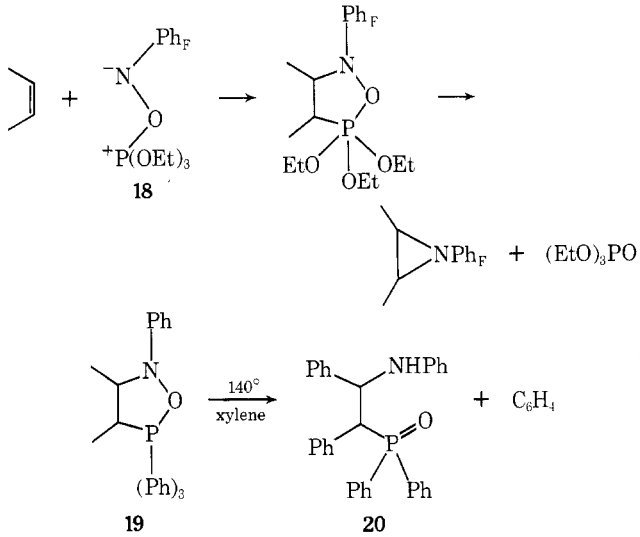

14




**15**, $R_1 = R_2 = R_3 = R_4$ = Me
**16**, $R_1 = R_2$ = Me; $R_3 = R_4$ = H
**17**, $R_1 = R_4$ = Me; $R_2 = R_3$ = H

30.5% yields, respectively. The $^1H$ NMR spectrum of **15** showed only one signal, a narrow triplet ($J$ = 1.7 Hz) at $\delta$ 1.30. The coupling is probably due to through-space interaction with the ortho fluorine substituents of the aromatic ring, since an authentic sample of *N-tert*-butylpentafluoroaniline, prepared from hexafluorobenzene and *tert*-butylamine, exhibited a similar splitting of the signal due to the methyl groups. Models of both these compounds confirmed that the methyl protons and ortho fluorines come into very close proximity to one another when the bonds are suitably rotated. The possibility that **15** might be formed from hydroxylamine **4** was eliminated by showing that **4** was stable to triethyl phosphite under the reaction conditions.

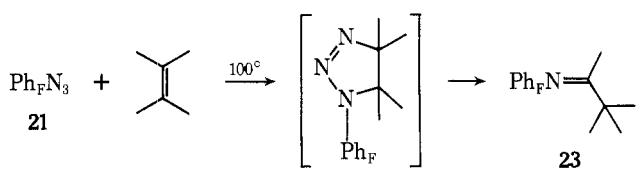
Reaction with *cis*- and *trans*-2-butene in a similar manner gave, along with **14**, the respective aziridines **16** and **17**. The reaction proceeded stereospecifically. In the NMR spectrum, the three-membered ring protons of **16** gave rise to a multiplet at $\delta$ 2.33 while those of **17** gave a signal at $\delta$ 2.28. That the trans aziridine (**17**) should give rise to a signal for the ring protons at *higher* field is in good agreement with the published data for *N*-acyl-2,3-dialkylaziridines.[17] The complete stereospecificity of the reaction thus demonstrated tends to rule out any stepwise diradical process, such as might be expected if a triplet nitrene were involved,[5] but does not exclude the possibility of dipolar addition of the nitrenoid **18** followed by extrusion of triethyl



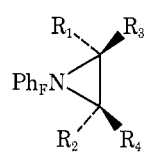
phosphate, in a manner analogous to the thermal extrusion of nitrogen from triazolines. This possibility was closely scrutinized.

Huisgen has reported the isolation of a closely related species, **19**, and shown it to be stable at room temperature,[18] whereas our reaction proceeds spontaneously, even at −78°. In addition, **19** undergoes thermal decomposition in boiling xylene to give **20**, no aziridine being formed. Furthermore, if the reactive intermediate in the deoxygenation were indeed a dipolar species, then it would be expected to be more reactive toward good dipolarophiles, such as methyl acrylate, than toward nonpolar olefins such as the butenes. In fact, when **1** was deoxygenated in the presence of excess methyl acrylate or dimethyl maleate, no adduct could be detected, the only isolable product being **14**. This behavior should be contrasted with the reaction between phenyl azide and methyl acrylate, a known 1,3-dipolar cycloaddition, which takes place under mild conditions to give a 1,2,3-triazoline in high yield.[19a] Deoxygenation of *p*-trifluoromethylnitrosobenzene with $(EtO)_3P$ in the presence of tetramethylethylene did not yield in aziridine. A low yield of 4,4′-di(trifluoromethyl)azoxybenzene was isolated.[19b]

When pentafluorophenyl azide (**21**) was heated at 100° in tetramethylethylene, the expected[20] triazoline **22** was not obtained. Instead, extrusion of nitrogen was accompanied by rearrangement, resulting in the imine **23**. Oehlschlager and Zalkow have reported similar rearrangements in related systems.[21] **23** gave pentafluoroaniline and *tert*-butyl methyl ketone on acid hydrolysis. On the other hand, photolysis of **21** in tetramethylethylene (below the temperature at which 1,1-dipolar addition occurs) gave **15** in 60% yield, and in *cis*- and *trans*-2-butene gave **16** and **17**, respectively, and stereospecifically, each in 18% yield.



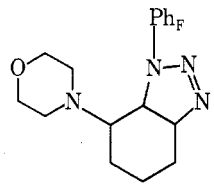

These observations strongly suggest the participation of a common intermediate in the deoxygenation and azide photolysis reactions but not in the azide thermolysis, and this is most likely the corresponding singlet nitrene. Other comparison between the nitroso compound deoxygenations and azide photolyses provided further evidence. Thus, cyclohexene gave the expected aziridine, **24**, in 35 and 39% yields, respectively. Likewise, stereospecific aziridine formation occurred when **21** was photolyzed in *cis*- and *trans*-1,2-dichloroethylene, a substrate with which no thermal reaction occurred, even at 100°. An aziridine was also obtained with 4-methyl-2-pentene but no reaction occurred with the highly deactivated trichloroethylene.



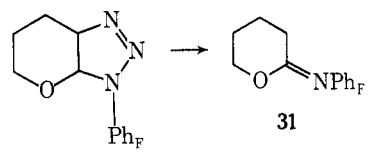

**24**, $R_1 = R_2 = H$; $R_3R_4 = -(CH_2)_4-$
**25**, $R_1 = R_2 = H$; $R_3 = R_4 = Cl$
**26**, $R_1 = R_4 = H$; $R_2 = R_3 = Cl$
**27**, $R_1 = R_2 = H$; $R_3 = R_4 = Ph$
**28**, $R_1 = R_4 = H$; $R_2 = R_3 = Ph$

Reactions with aryl-substituted ethylenes showed more variations. Deoxygenation of **1** in the presence of *trans*-stilbene gave the expected single aziridine **28** in 32% yield, but with *cis*-stilbene only 0.6% of the geometrically isomeric aziridine **27** was isolated. Photolysis of **21** in the presence of stilbenes gave no adducts at all; this might be due to absorption of the radiation by the olefinic substrate which was present in high relative concentration in these experiments.

Reaction of the enamine **8** with **1** proved to be more rapid than the deoxygenation of **1** by triethyl phosphite inasmuch as, even at low temperature, only **9** was isolated. Reaction of **8** with **21** also occurred rapidly at room temperature to give triazoline **29** with the expected orientation.[22]

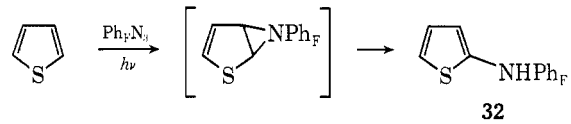



Vinyl ethers are known to display similar activity toward aryl azides.[23] The primary adducts formed in such reactions usually eliminate a molecule of nitrogen to give an aziridine, but when the nitrogen atom bears a strongly electronegative substituent, an imine results from loss of nitrogen.[24] The latter was observed when **21** was added to dihydropyran, **31** being the product isolated, presumably via **30**.



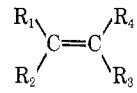

These observations precluded an investigation of the behavior of enamines and vinyl ethers toward aryl nitrenes generated under the conditions used in this paper.

Irradiation of ethyl azidoformate in the presence of certain five-membered aromatic heterocycles has been reported to give both 1,2 and 1,4 adducts via a nitrene intermediate.[7a,25] Irradiation of **21** in pyrrole gave only tars, but in thiophene the apparent substitution product **32** was obtained, probably formed via the initial addition of $C_6F_5N$ as in the case of benzene derivatives.[12]



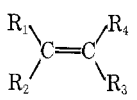

In an extension of the studies with pentafluorophenylnitrene the properties of 2- and 4-azidotetrachloropyridine were investigated briefly. After this work was completed, a report appeared[26] on the chemistry of 4-azidotetrafluoropyridine, whose derived nitrene is also highly electrophilic in character. 4-Azidotetrachloropyridine, synthesized from pentachloropyridine and sodium azide, readily underwent thermal cycloaddition to tetramethylethylene to give eventually the imine **33** (cf. formation of **23**) in 79% yield. The reaction was slow at room temperature, however, and photolysis under these conditions resulted in formation of the aziridine **34** in 14% yield, along with a small amount of the hydrogen abstraction product **35**. The latter could arise from the triplet nitrene. Photolysis of 4-azidotetrachloropyridine in cyclohexene gave only amine **35**, no adduct being formed, suggesting that the derived nitrene is much less electrophilic than the corresponding fluorinated species, as expected. 2-Azidotetrachloropyridine gave only

**Table I**
**Deoxygenation of Pentafluoronitrosobenzene with Triethyl Phosphite in**



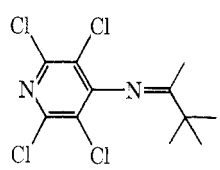
| Registry no. | $R_1$ | $R_2$ | $R_3$ | $R_4$ | Temp, °C | Aziridine, % | **14**, % |
|---|---|---|---|---|---|---|---|
| 563-79-1 | Me | Me | Me | Me | −10 | 30 | 14 |
| 590-18-1 | H | Me | Me | H | −20 | 17 | 27 |
| 624-64-6 | Me | H | Me | H | −20 | 18 | 35 |
| 110-83-8 | H | $-(CH_2)_4-$ | | H | 0 | 35 | 13 |
| 103-30-0 | Ph | H | Ph | H | −20 | 26 | |
| 645-49-8 | H | Ph | Ph | H | −45 | 1 | |
| 624-48-6 | H | $CO_2Me$ | $CO_2Me$ | H | −40 | | 48 |
| 96-33-3 | $CO_2Me$ | H | H | H | −45 | | 53 |

**Table II**
**Photolysis of $Ph_FN_3$ at 300 nm in**

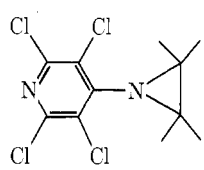


| Registry no. | $R_1$ | $R_2$ | $R_3$ | $R_4$ | Time, hr | Aziridine, % |
|---|---|---|---|---|---|---|
| | Me | Me | Me | Me | 48 | 60 |
| | H | Me | Me | H | 48 | 18 |
| | Me | H | Me | H | 85 | 18 |
| 156-59-2 | H | Cl | Cl | H | 6 days | 21 |
| 156-60-5 | Cl | H | Cl | H | 168 | 27 |
| | H | $-(CH_2)_4-$ | | H | 12 | 39 |
| 1674-10-8 | Me | $-(CH_2)_4-$ | | Me | 70 | 11 |
| 691-38-3 | Me | H | *i*-Pr | H | 88 | 20 |
| | Ph | H | Ph | H | | |
| | H | Ph | Ph | H | | |

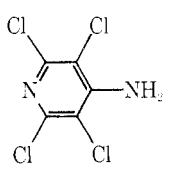
tars when heated in tetramethylethylene, but did yield a triazole (**36**) (82%) with dimethyl acetylenedicarboxylate.



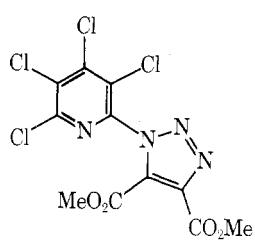
**33**



**34**



**35**



**36**

The addition of pentafluorophenylnitrene to olefins is summarized in Tables I and II.

## Experimental Section

**General.** Melting points are uncorrected and were taken on an Electrothermal apparatus; infrared spectra were determined on a Perkin-Elmer 257, NMR spectra on a Varian HA-100 or Hitachi R-20B, and mass spectra on a CEC-104 instrument. Silica gel for column chromatography was Baker 60–200 mesh. Silica gel for TLC was Merck $PF_{254}$. Light petroleum refers to the fraction of bp 30–60°. Drying of solutions was invariably with anhydrous sodium sulfate.

Pentafluoronitrosobenzene was prepared by performic acid oxidation of pentafluoroaniline and purified by distillation according to the method of Tatlow.[27] Pentafluorophenyl azide was prepared by diazotization of pentafluorophenyl hydrazine,[28] or by reaction of hexafluorobenzene with sodium azide in dimethyl sulfoxide.[29] Photolyses were carried out in a Rayonet photochemical reactor.

**Reaction of Pentafluoronitrosobenzene and Other Nitrosobenzenes with Tetramethylethylene.** Pentafluoronitrosobenzene (140 mg) was added to excess tetramethylethylene and shaken until dissolved. Evaporation of the excess olefin gave colorless crystals of ***N*-(1,1,2-trimethyl)-2-propenylpentafluorophenylhydroxylamine** (191 mg, 96%): mp 78–79° (light petroleum); ir (KBr) 3310 (br), 1636, 1490, 1372, 1362, 1150, 1140, 990, 962, 900 $cm^{-1}$; NMR ($CCl_4$) δ 5.40 (s, 1, exchanged with $D_2O$), 5.00 (m, 2), 1.93 (s, 3), 1.27 (t, $J$ = 1.7 Hz, 6); MS *m/e* (rel abundance) 281 (1), 280 (1), 265 (2), 263 (3), 250 (2), 224 (8), 208 (9), 197 (3), 183 (9), 167 (3), 117 (10), 83 (100).

Anal. Calcd for $C_{12}H_{12}F_5NO$: C, 51.21; H, 4.27. Found: C, 51.19; H, 4.36.

Catalytic reduction over 10% Pd/C in ether at 25° (1 atm) gave the saturated side-chain molecule as an oil, bp 120–122° (1 mm), MS *m/e* 240 ($M^{\cdot+}$ − F), 85 (100).

Anal. Calcd for $C_{12}H_{14}F_5NO$: C, 50.88; H, 4.95. Found: C, 51.16; H, 5.11.

A similar reaction using nitrosobenzene gave analytically pure **3** in 77% yield after one recrystallization, mp 59–60° (light petroleum) (lit.[15b] mp 58°).

Addition of *p*-nitrosobenzotrifluoride to tetramethylethylene gave ***N*-(1,1,2-trimethyl-2-propenyl)-4-trifluoromethylphenylhydroxylamine** (85%), mp 76–77° (light petroleum).

Anal. Calcd for $C_{13}H_{16}F_3NO$: C, 60.22; H, 6.18. Found: C, 60.12; H, 6.28.

**Reaction of Pentafluoronitrosobenzene with 2-Butenes.** Pentafluoronitrosobenzene (141 mg) and *cis*-2-butene (3 ml) in methylene chloride (3 ml) was allowed to stand at −20° for 2 hr, after which the solvents were evaporated and the residue was recrystallized from light petroleum to give ***N*-(1-methyl)-2-propenylpentafluorophenylhydroxylamine** (109 mg, 60%): mp 72–73°; ir (NaCl) 3295, 1643, 1500, 1370, 1328, 1070, 990, 946, 830 $cm^{-1}$; NMR ($CCl_4$) δ 6.39 (s, 1, exchanged with $D_2O$), 5.54–6.13 (q, 1), 5.20 (dd, $J$ = 4 Hz, 1), 3.75–4.22 (q, 1), 1.28 (d, $J$ = 7 Hz, 3); MS *m/e* (rel abundance) 253 ($M^{\cdot+}$, 0.3), 252 (1), 220 (2), 208 (2), 197 (6), 194 (10), 182 (2), 167 (5), 117 (8), 93 (4), 55 (100).

Anal. Calcd for $C_{10}H_8F_5NO$: C, 47.44; H, 3.16. Found: C, 47.90; H, 3.33.

TLC of the mother liquors gave **36** (8 mg) as an oil.

Reaction under the same conditions with *trans*-2-butene gave an oily residue which was subjected to preparative TLC and elution with $CHCl_3$–light petroleum (1:9 v/v) to give *N*-(1-methyl)-2-propenylpentafluoroaniline (44 mg, 8.5%) (**6**): ir (film) 3375, 3078, 1650, 1513, 1372, 1351, 1260, 1020, 989, 926 $cm^{-1}$; NMR ($CCl_4$) δ 5.52–6.08 (septet, 1), 5.22 (dd, $J$ = 8 and 2 Hz, 1), 5.00 (d, $J$ = 4 Hz, 1), 4.23 (m, 1), 3.40 br (s, 1, exchanged with $D_2O$), 1.36 (d, $J$ = 7 Hz, 3); MS *m/e* (rel abundance) 237 ($M^{\cdot+}$, 6), 222 (6), 195 (30), 183 (22), 181 (98), 167 (100), 155 (26), 131 (76), 117 (92), 93 (49), 69 (35).

**Reaction of 1 with 1-(*N*-Morpholino)-1-cyclohexene.** Pentafluoronitrosobenzene (890 mg) in methylene chloride was added to 1-(*N*-morpholino)-1-cyclohexene (734 mg) in methylene chloride (10 ml) and stirred for 1 hr at 25°. Removal of the solvent gave a residue of **1-(*N*-morpholino)-6-(*N*-pentafluorophenylhydroxylamino)-1-cyclohexene (9,** 601 mg, 40%): mp 95–96° (light

petroleum); ir (KBr) 3290, 1640, 1500, 990 $cm^{-1}$; MS *m/e* (rel abundance) 364 ($M\cdot^+$, 2), 167 (100), 166 (98), 86 (17), 80 (12).

Anal. Calcd for $C_{16}H_{17}F_5N_2O_2$: C, 52.76; H, 4.68. Found: C, 52.59; H, 4.81.

Similar results were obtained when the reaction was carried out in the presence of triethyl phosphite (see general conditions below) at −40° (yield of hydroxylamine 34%). No aziridine was observed under these conditions.

**Hydrolysis of 9.** A mixture of **9** (0.24 g) in methylene chloride (5 ml) and 10% HCl (7 ml) was stirred at room temperature for 72 hr. Extraction with $CH_2Cl_2$, washing with water, drying ($Na_2SO_4$), and evaporation gave **2-*N*-pentafluorophenylhydroxylaminocyclohexanone** (**11,** 0.13 g, 70%), mp 117–118° (ether): ir (KBr) 3480, 1710, 1495, and 990 $cm^{-1}$; MS *m/e* (rel abundance) 294 ($M\cdot^+$, 11), 167 (22), 127 (55), 97 (100).

Anal. Calcd for $C_{12}H_{10}F_5NO_2$: C, 49.00; H, 3.10. Found: C, 48.99; H, 3.21.

**Reaction of 1 with Cyclohexene.** Pentafluoronitrosobenzene (255 mg) in $CH_2Cl_2$ (2 ml) was added over 0.5 hr to a stirred solution of cyclohexene (2 ml) in $CH_2Cl_2$ (3 ml) at 30° under $N_2$. After stirring for a further 0.5 hr the solvents were evaporated and the residue was subjected to preparative TLC. Elution with benzene–light petroleum (1:3 v/v) gave ***N*-(3-cyclohexenyl)pentafluoroaniline** (39 mg, 11.4%): bp 70–75° (0.1 mm); ir (film) 3390 $cm^{-1}$; NMR ($CCl_4$) δ 5.82 (m, 2), 4.14 (s, 1, exchanged with $D_2O$), 3.43 (m, 1), 2.03 (m, 2), 1.76 (m, 4); MS *m/e* (rel abundance) 263 ($M\cdot^+$, 9), 81 (100).

Anal. Calcd for $C_{12}H_{10}F_5N$: C, 54.80; H, 3.80. Found: C, 55.01; H, 3.64.

Further elution gave an unidentified yellow oil (10 mg) [ir (film) 1723, 1674, 1642, and 1324 $cm^{-1}$] and intractable oils and gums.

**Deoxygenation of Pentafluoronitrosobenzene in Tetramethylethylene.** Pentafluoronitrosobenzene (575 mg) in chlorobenzene (2 ml) was added dropwise to a stirred solution of triethyl phosphite (485 mg) in tetramethylethylene (3 g) at −10°. The resulting brown solution was evaporated down to a small volume and the residue was chromatographed on silica gel (5 × 20 cm). Elution with light petroleum gave chlorobenzene. Elution with light petroleum–benzene (4:1 v/v) gave an oil which crystallized on standing to **2,2,3,3-tetramethyl-1-pentafluorophenylaziridine** (235 mg, 30.5%): mp 70–72° (light petroleum); ir (KBr) 1498, 1440, 1377, 1201, 1172, 1035, 986, 790 $cm^{-1}$; NMR ($CCl_4$) δ 1.30 (t, $J$ = 1.7 Hz); MS *m/e* (rel abundance) 265 ($M\cdot^+$, 7), 250 (9), 223 (7), 208 (48), 196 (6), 183 (100), 167 (7), 155 (21), 136 (26), 117 (21), 83 (24), 82 (26), 67 (40), 41 (22).

Anal. Calcd for $C_{12}H_{12}F_5N$: 54.38; H, 4.53. Found: C, 54.43; H, 4.60.

Further elution with light petroleum–benzene (1:4 v/v) gave decafluoroazoxybenzene (77 mg, 14.0%), mp 52–54°, identical with an authentic sample.[11] Elution with benzene–light petroleum (1:1 v/v) gave **4** (45 mg, 5.5%), mp 77–79°.

Similarly prepared were the following.

***trans*-2,3-Dimethyl-1-pentafluorophenylaziridine** (18.0%): bp 70–75° (1.5 mm); ir (film) 2990, 1500, 1450, 1380, 1170, 1104, 1038, 987 $cm^{-1}$; NMR ($CCl_4$) δ 2.28 (br q, $J$ = 5 Hz, 2), 1.30 (d, $J$ = 5 Hz, 6); MS *m/e* (rel abundance) 237 ($M\cdot^+$, 34), 222 (22), 208 (25), 195 (100), 194 (90), 181 (27), 167 (60), 117 (59).

Anal. Calcd for $C_{10}H_8F_5N$: C, 50.63; H, 3.38. Found: C, 50.68; H, 3.47.

***cis*-2,3-Dimethyl-1-pentafluorophenylaziridine** (17.3%): mp 68–70° (sublimed in vacuo); ir (NaCl) 2990, 1503, 1460, 1307, 1172, 1078, 1026, 988 $cm^{-1}$; NMR ($CCl_4$) δ 2.33 (m, 2), 1.34 (d, $J$ = 5 Hz, 6); MS *m/e* (rel abundance) 237 ($M\cdot^+$, 34), 222 (27), 208 (30), 195 (100), 194 (92), 167 (49), 117 (52).

Anal. Calcd for $C_{10}H_8F_5N$: C, 50.63; H, 3.38. Found: C, 50.57; H, 3.45.

**7-Pentafluorophenyl-7-azabicyclo[4.1.0]heptane** (35.0%): bp 55–60° (0.5 mm); ir (film) 1500, 1191, 1032, 1008, 978, 941, 814 $cm^{-1}$; NMR ($CCl_4$) δ 2.96 (m, 2), 2.50 (br d, 4), 1.9–2.1 (m, 4); MS *m/e* (rel abundance) 263 ($M\cdot^+$, 16), 181 (64), 167 (70), 131 (62), 117 (69), 81 (100).

Anal. Calcd for $C_{12}H_{10}F_5N$: C, 54.76; H, 3.80. Found: C, 54.77; H, 3.80.

***trans*-2,3-Diphenyl-1-pentafluorophenylaziridine** (26.0%): mp 88–89° (light petroleum); ir (KBr) 1600, 1510, 1450, 1187, 1068, 1000, 812, 750, 697 $cm^{-1}$; NMR ($CCl_4$) δ 7.30 (s, 10), 3.85 (t, $J$ = 1.7 Hz, 2); MS *m/e* (rel abundance) 361 ($M\cdot^+$, 72), 360 (54), 270 (28), 257 (28), 194 (42), 178 (46), 167 (100), 152 (28), 117 (29), 77 (95).

Anal. Calcd for $C_{20}H_{12}F_5N$: C, 66.50; H, 3.33. Found: C, 66.57; H, 3.40.

**Deoxygenation of Pentafluoronitrosobenzene in *cis*-Stilbene.** Pentafluoronitrosobenzene (723 mg) in methylene chloride (10 ml) was added dropwise to a stirred solution of *cis*-stilbene (1.62 g) and triethyl phosphite (604 mg) in methylene chloride (40 ml) at −45°. After a further 5 min, the solvent was evaporated and the residue was chromatographed on silica gel (5 × 20 cm). Elution with light petroleum–benzene (9:1 v/v) gave recovered *cis*-stilbene and a fraction showing additional infrared absorptions to those of *cis*-stilbene. On prolonged standing, this fraction deposited crystals of ***cis*-2,3-diphenyl-1-pentafluorophenylaziridine** (6 mg, 0.6%): mp 113–115° (light petroleum); ir (KBr) 3020, 1490, 1450, 1390, 1045, 1000, 975, 760, 745, 690 $cm^{-1}$; NMR ($CCl_4$) δ 7.07 (s, 10), 3.65 (br s, 2) ; MS *m/e* (rel abundance) 361 ($M\cdot^+$, 5), 360 (5), 194 (13), 181 (39), 180 (100), 179 (92), 167 (63), 89 (37), 77 (34).

Anal. Calcd for $C_{20}H_{12}NF_5$: mol wt, 361.0887. Found: mol wt, 361.0905.

**Deoxygenation of Pentafluoronitrosobenzene in Dimethyl Maleate.** A solution of pentafluoronitrosobenzene (0.99 g) in methylene chloride (10 ml) was added quickly at −40° to a solution of dimethyl maleate (1.75 g) and triethyl phosphite (0.83 g) in methylene chloride (20 ml). A brown solution resulted. After 5 min the solvent was evaporated and the residual oil was chromatographed on a column of silica gel (100 g) to give decafluoroazoxybenzene (0.46 g, 48%), mp 53–54°, undepressed on admixture with an authentic sample.

A similar result was obtained when methyl acrylate and *n*-butyl vinyl ether were used as the substrates. The yields of azoxy compound were 53.0 and 10.4%, respectively.

**Deoxygenation of *p*-Trifluoromethylnitrosobenzene in Tetramethylethylene.** To a cold solution (0°) of tetramethylethylene (6 ml) and triethyl phosphite (0.86 g) was rapidly added a solution of *p*-trifluoronitrosobenzene (0.92 g) in methylene chloride (3 ml). After 30 min the solution was worked up and the product was chromatographed on a column of silica gel (30 g) to give 4,4′-trifluoromethylazoxybenzene (0.11 g, 12%), mp 103–105°, identical with an authentic sample.

When the reaction was carried out at −50° the yield of azoxy compound was 23.1%.

**Decomposition of Pentafluorophenyl Azide in Tetramethylethylene and other Olefins. A. Thermolysis.** Pentafluorophenyl azide (424 mg) in tetramethylethylene (10 ml) was degassed and then heated in a sealed tube at 100° for 48 hr. Excess olefin was evaporated from the cooled mixture and the residue was distilled to give **2,2-dimethyl-3-pentafluorophenyliminobutane** (**23,** 496 mg, 97%): bp 65° (0.5 mm); ir (film) 2960, 1650, 1505, 1370, 1150, 1145, 1000, 950, 840 $cm^{-1}$; NMR ($CCl_4$) δ 1.84 (s, 3), 1.27 (s, 9); MS *m/e* (rel abundance) 265 ($M\cdot^+$, 12), 250 (9), 209 (14), 208 (100), 183 (11), 167 (14), 117 (12), 57 (21).

Anal. Calcd for $C_{12}H_{12}F_5N$: C, 54.43; H, 4.51. Found: C, 54.40, H, 4.55.

A solution of **23** (353 mg), methanol (1 ml), and 25% sulfuric acid (5 ml) was stirred at 25° for 72 hr, after which the mixture was extracted with methylene chloride and the extracts were washed with water and dried. Evaporation of the solvent gave a residue shown to contain pinacolone and pentafluoroaniline by GLC analysis and comparison with authentic samples.

**B. Photolysis.** Pentafluorophenyl azide (436 mg) in tetramethylethylene (10 ml) was degassed and then photolysed in a sealed Pyrex tube with 300-nm radiation at 25° for 48 hr. The solvent was then evaporated and the crystalline residue, after preparative TLC and elution with benzene–light petroleum (1:4 v/v), gave 2,2,3,3-tetramethyl-1-pentafluorophenylaziridine (336 mg, 60%), mp 70–72° (light petroleum), identical with the previously prepared sample.

Similarly prepared were the following.

*cis*- and *trans*-2,3-dimethyl-1-pentafluorophenylaziridine (18.0 and 18.0%) (from *cis*- and *trans*-2,3-dimethyl-2-butene, respectively), and 7-pentafluorophenyl-7-azabicyclo[4.1.0]heptane (38.6%) (from cyclohexene), all identical with previously prepared compounds.

***cis*-2,3-Dichloro-1-pentafluorophenylaziridine** (27.0%): mp 124–125° (light petroleum) (from *cis*-dichloroethylene); ir (KBr) 1520, 1350, 1090, 1005, 870, 855, 710 $cm^{-1}$; NMR ($CCl_4$) δ 4.54 (dd, $J$ = 0.75 Hz); MS *m/e* (rel abundance) 281 ($M\cdot^+$, $^{37}Cl_2$, 1.5), 279 ($^{37}Cl^{35}Cl$, 9), 277 ($M\cdot^+$, $^{35}Cl_2$, 14), 244 (12), 242 (30), 217 (6), 207 (15), 194 (100), 174 (15), 167 (33), 117 (42), 93 (70).

Anal. Calcd for $C_8H_2Cl_2F_5N$: C, 34.53; H, 0.72. Found: C, 34.57; H, 0.80.

***trans*-2,3-Dichloro-1-pentafluorophenylaziridine** (21.0%): mp 54–56° (light petroleum) (from *trans*-dichloroethylene); ir

(NaCl) 1500, 1320, 1260, 1250, 1093, 1050, 890, 840, 810, 775 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 4.70 (m); MS *m/e* (rel abundance) 281 ($M\cdot^+$, $^{37}Cl_2$, 1), 279 ($^{37}Cl^{35}Cl$, 6), 277 ($M\cdot^+$, $^{35}Cl_2$, 10), 244 (16), 207 (8), 194 (50), 181 (8), 167 (33), 117 (33), 109 (100), 83 (33).

Anal. Calcd for $C_8H_2Cl_2F_5N$: C, 34.53; H, 0.72. Found: C, 34.47; H, 0.78.

**1,6-Dimethyl-7-pentafluorophenyl-7-azabicyclo[4.1.0]heptane** (11.3%): mp 42–43° (light petroleum) (from 1,2-dimethylcyclohexene); ir (KBr) 2940 1510, 1450, 1395, 1205, 1150, 1060, 1000, 800 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.32–2.2 (br d, 8), 1.19 (t, $J$ = 3 Hz, 6); MS *m/e* (rel abundance) 291 ($M\cdot^+$, 12), 276 (12), 209 (100), 167 (50), 117 (52).

Anal. Calcd for $C_{14}H_{14}F_5N$: mol wt, 291.1047. Found: mol wt, 291.1042.

***trans*-2-Methyl-3-isopropyl-1-pentafluorophenylaziridine** (19.7%): bp 90–100° (0.5 mm) (from 2-methyl-3-pentene); ir (film) 2970, 1500, 1170, 1040, 990 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 2.50 (br d, 1), 1.95 (m, 11), 1.60 (m, 1), 1.19 (d, $J$ = 4.5 Hz, 6), 1.08 (s, 3), 0.96 (s, 2); MS *m/e* (rel abundance) 265 ($M\cdot^+$, 11), 250 (26), 211 (22), 196 (100), 167 (22), 117 (22), 84 (16).

Anal. Calcd for $C_{12}H_{12}F_5N$: C, 54.34; H, 4.53. Found: C, 54.50; H, 4.58.

**Thermolysis of Pentafluorophenyl Azide in Dihydropyran.** Pentafluorophenyl azide (326 mg) and dihydropyran (2.5 g) were sealed in a Pyrex tube and heated at 120° for 24 hr. Excess dihydropyran was removed from the cooled mixture, leaving an oil which crystallized to give **$\delta$-valerolactone pentafluoroanil** (208 mg, 70%): mp 57–59° (light petroleum); ir (KBr) 2960, 1650, 1500, 1400, 1340, 1280, 1255, 1080, 1000 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 4.20 (t, $J$ = 5 Hz, 2), 2.70 (t, $J$ = 5 Hz, 2), 1.95 (m, 4); MS *m/e* (rel abundance) 265 ($M\cdot^+$, 10), 181 (100), 153 (11), 135 (20), 116 (20).

Anal. Calcd for $C_{11}H_8F_5NO$: C, 49.80; H, 3.02. Found: C, 49.83; H, 3.07.

The same product was also obtained (90%) when the reaction was conducted at 25° for 12 days.

**Photolysis of Pentafluorophenyl Azide in Thiophene.** Pentafluorophenyl azide (326 mg) in thiophene (10 ml) was sealed in a Pyrex tube and irradiated at 300 nm at 25° for 64 hr. The excess thiophene was then evaporated and the residue was subjected to preparative TLC. Elution with light petroleum gave **2-pentafluoroanilinothiophene** (48 mg, 11.5%): mp 55–60° (light petroleum); ir (KBr) 3400, 1525, 1090, 1020, 820, 790 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 7.17 (dd, $J$ = 4 and 3 Hz, 1), 6.79 (d, $J$ = 4 Hz, 1); MS *m/e* (rel abundance) 265 ($M\cdot^+$, 100), 246 (58), 245 (38), 220 (35), 201 (18), 174 (14), 168 (9), 167 (4), 117 (56), 99 (50), 71 (88).

Anal. Calcd for $C_{10}H_4F_5NS$: C, 46.00; H, 1.51. Found: C, 46.01; H, 1.58.

**4-Azidotetrachloropyridine.** Pentachloropyridine (2.5 g) and sodium azide (1.0 g) were heated in boiling acetonitrile (50 ml) for 10 hr. The mixture was poured into water and extracted with chloroform. Drying and evaporation of the chloroform extracts gave a yellow oil, which was subjected to preparative TLC. Elution with light petroleum gave starting material (1.7 g) and **4-azidotetrachloropyridine** (0.80 g, 22.1%): mp 47–48° (light petroleum); ir (KBr) 2150, 1525, 1400, 1355, 1330, 1185, 1110, 920, 900, 765 $cm^{-1}$.

Anal. Calcd for $C_5Cl_4N_4$: C, 23.25; H, 0.0. Found: C, 23.43; H, 0.0.

**Decomposition of 4-Azidotetrachloropyridine in Tetramethylethylene. A. Thermolysis.** 4-Azidotetrachloropyridine (463 mg) in tetramethylethylene (5 ml) was heated at 120° in a sealed tube for 24 hr. Excess olefin was evaporated and the residue was subjected to preparative TLC. Elution with light petroleum gave **2,2-dimethyl-3-(4-tetrachloropyridyl)iminobutane** (454 mg, 79.5%): mp 100–101° (light petroleum); ir (KBr) 2990, 1670, 1530, 1375, 1350, 1320, 1250, 1155, 1000, 940, 850, 785, 735 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 1.80 (s, 3), 1.28 (s, 9); MS *m/e* (rel abundance) 320 ($M\cdot^+$, $^{37}Cl_4$, 0.1), 318 ($^{37}Cl_3{}^{35}Cl$, 0.7), 316 ($^{37}Cl_2{}^{35}Cl_2$), 314 ($^{37}Cl^{35}Cl_3$, 7), 312 ($M\cdot^+$, $^{35}Cl_4$, 5), 273 (9), 271 (14), 258 (42), 256 (100), 254 (72), 214 (14), 117 (14).

Anal. Calcd for $C_{11}H_{12}Cl_4N_2$: C, 42.04; H, 3.82. Found: C, 42.20; H, 3.88.

**B. Photolysis.** 4-Azidotetrachloropyridine (487 mg) in tetramethylethylene (5 ml) was irradiated at 300 nm in a sealed tube for 6.5 days at 25°. Excess olefin was evaporated and the residue was subjected to preparative TLC. Elution with light petroleum gave **2,2,3,3-tetramethyl-1-(4-tetrachloropyridyl)aziridine** (85 mg, 14.3%): mp 151–152° (light petroleum); ir (KBr) 2940, 1525, 1510, 1430, 1340, 1245, 1205, 1120, 1050, 990, 800, 750 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.40 (s); MS *m/e* (rel abundance) 320 ($M\cdot^+$, $^{37}Cl_4$, 0.2) 318 ($^{37}Cl_3{}^{35}Cl$, 2), 316 ($^{37}Cl_2{}^{35}Cl_2$, 11), 314 ($^{37}Cl^{35}Cl_3$, 22), 312 ($M\cdot^+$, $^{35}Cl_4$, 17), 280 (61), 278 (56), 268 (44), 266 (100), 264 (78), 247 (22), 245 (22), 216 (28), 214 (17), 181 (11), 154 (22), 153 (28), 144 (17), 118 (17).

Anal. Calcd for $C_{11}H_{12}Cl_4N_2$: C, 42.04; H, 3.82. Found: C, 41.98; H, 3.83.

Also eluted was 4-aminotetrachloropyridine (6.1 mg, 1.4%), mp 215–216° (lit.[30] mp 212–215°).

When the photolysis was carried out in cyclohexene the only isolable product was the primary amine (12.1%), mp 212–214°.

**Thermolysis of 2-Azidotetrachloropyridine in Dimethyl Acetylenedicarboxylate.** 2-Azidotetrachloropyridine[30] (627 mg) and dimethyl acetylenedicarboxylate (503 mg) were heated in boiling chloroform for 43 hr. Evaporation of the solvent gave a residue which was subjected to preparative TLC. Elution with light petroleum gave **4,5-dimethoxycarbonyl-1-(2-tetrachloropyridyl)-1,2,3-triazole** (814 mg, 85.2%): mp 125–126° [chloroform–light petroleum (1:1 v/v)]; ir (KBr) 2960, 1750, 1725, 1590, 1530, 1450, 1330, 1300, 1260, 1230, 1140, 110, 970, 840, 810, 770 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 4.00 (s, 3), 3.90 (s, 3); MS *m/e* (rel abundance) 378 ($M\cdot^+$, $^{37}Cl_4$, 0.2), 376 ($^{37}Cl_3{}^{35}Cl$, 1.5), 374 ($^{37}Cl_2{}^{35}Cl_2$, 6), 372 ($^{37}Cl^{35}Cl_3$, 6), 370 ($M\cdot^+$, $^{35}Cl_4$, 9), 340 (12), 285 (50), 272 (18), 257 (18), 255 (31), 253 (25), 219 (50), 216 (100), 214 (75), 181 (37), 179 (43), 155 (25), 153 (25), 144 (19), 109 (25).

Anal. Calcd for $C_{11}H_6Cl_4N_4O_4$: C, 33.00; H, 1.50. Found: C, 33.10; H, 1.61.

***N*-*tert*-Butylpentafluoroaniline.** Hexafluorobenzene (5 g), *tert*-butylamine (3.7 g), and sodium carbonate (2.5 g) were heated in a sealed tube at 100° for 14 hr. The cooled, filtered mixture was evaporated to give ***N*-*tert*-butylpentafluoroaniline** (0.7 g, 11%): bp 130–135° (20 mm); ir (film) 3400, 3340, 1470, 1367 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 2.95 (br s, 1, exchanged with $D_2O$), 1.28 (t, $J$ = 1.7 Hz, 9).

Anal. Calcd for $C_{10}H_{10}F_5N$: C, 50.18; H, 4.19. Found: C, 50.19; H, 4.33.

**Registry No.**—**1,** 1423-13-8; **3,** 28943-93-3; **4a,** 30287-20-8; **4b,** 54698-78-1; **6,** 54698-79-2; **8,** 670-80-4; **9,** 54698-80-5; **11,** 54698-81-6; **15,** 39904-17-1; **16,** 39830-50-7; **17,** 39830-49-4; **21,** 1423-15-0; **23,** 54698-82-7; **25,** 54698-94-1; **26,** 54698-95-2; **27,** 54698-96-3; **28,** 39830-51-8; **32,** 54698-83-8; **33,** 54698-84-9; **34,** 54698-85-0; **36,** 54698-86-1; *N*-(1,1,2-trimethyl)propylpentafluorophenylhydroxylamine, 54698-87-2; *N*-(1-methyl)-2-propenylpentafluorophenylhydroxylamine, 54698-88-3; *N*-(3-cyclohexenyl)pentafluoroanilene, 54698-89-4; 7-pentafluorophenyl-7-azabicyclo[4.1.0]heptane, 54698-90-7; *p*-trifluoromethylnitrosobenzene, 34913-26-3; 1,6-dimethyl-7-pentafluorophenyl-7-azabicyclo[4.1.0]heptane, 54698-91-8; *trans*-2-methyl-3-isopropyl-1-pentafluorophenylaziridine, 54698-97-4; dihydropyran, 110-87-2; $\delta$-valerolactone pentafluoroanil, 54698-92-9; thiophene, 110-02-1; pentachloropyridine, 2176-62-7; 4-azidotetrachloropyridine, 51379-64-7; 2-azidotetrachloropyridine, 54698-93-0; dimethyl acetylenedicarboxylate, 762-42-5; *N*-*tert*-butylpentafluoroaniline, 13471-90-4; hexafluorobenzene, 392-56-3; *tert*-butylamine, 75-64-9; nitrosobenzene, 586-96-9.

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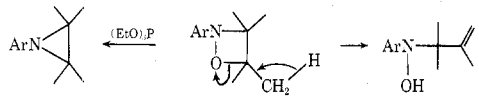

both *p*-trifluoromethylnitrosobenzene and PhNO give "ene"-type products with 2,3-dimethyl-2-butene they do not give any aziridine in the inverse addition in the presence of $(EtO)_3P$. That aziridines are also formed from $C_6F_5N_3$ by photolysis also supports the electrophilic nitrene hypothesis for the addition to olefinic double bonds.
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# Purine *N*-Oxides. LXI. 3-Hydroxy-2,3-dihydro-2-oxopurine[1]

Tzoong-Chyh Lee, Fuk Luen Lam, and George Bosworth Brown*

*Memorial Sloan-Kettering Cancer Center, New York, New York 10021*

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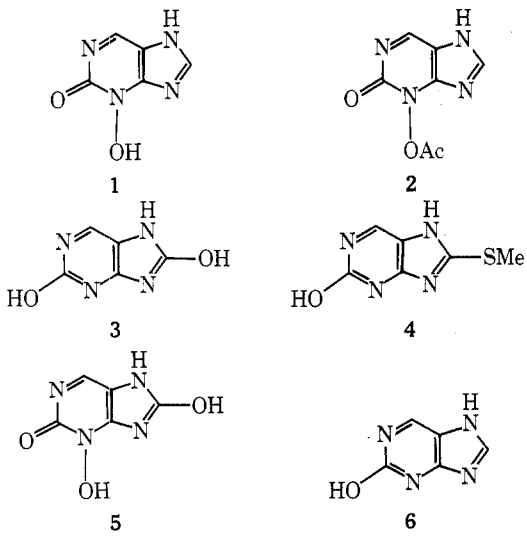
The synthesis and reactivity of 3-hydroxy-2,3-dihydro-2-oxopurine (1) is described. The acetyl and tosyl esters of 1 react with water to give some 2,8-dihydroxypurine and hydrolysis products, while the acetyl ester of 1 prepared in situ reacts with methionine at room temperature to give almost quantitative yield of 2-hydroxy-8-methylmercaptopurine. The xanthine oxidase oxidation of 1 gave good yield of 3,8-dihydroxy-2,3-dihydro-2-oxopurine. The photoirradiation of 1 at pH 3.0 produces 2-hydroxypurine (21%) and a small amount of 2,8-dihydroxypurine (1%), while at pH 9.0 it gives mostly a ring-opened imidazole derivative, a small amount of 2-hydroxypurine, and a trace of 2,8-dihydroxypurine.

It has been reported from this laboratory that esters of 3-hydroxyxanthine[2-6] and some of its methylated derivatives undergo an elimination–substitution reaction to yield 8-substituted xanthines, even at room temperature and in nearly neutral solution. The subsequent studies of some analogs[7-9] of 3-hydroxyxanthines have shown that some $\pi$-excessive ring systems can undergo an elimination–substitution reaction similar to that of the esters of 3-hydroxyxanthine.

This paper describes the reactions of 3-hydroxy-2,3-dihydro-2-oxopurine (1). This was prepared by condensation



of 5-aminocytosine 1-oxide[7] with triethyl orthoformate in boiling ethanol. Although the reaction was carried out heterogenously, the overall yield of 1 was found to be quite satisfactory. The identity of the compound was confimed by NMR, uv spectra, elemental analysis, and mass spectrum. The uv spectrum of 1 in both acid and neutral media resembles those of 2-hydroxypurine[10] (2,3-dihydro-2-oxopurine).[11,12] The uv of the neutral species of 1 shows a bathochromic shift of 5 nm in long-wavelength major band with respect to that of its parent purine, as do the uv spectra of 3-hydroxyxanthine and its analogs,[7-9] thus confirming that the neutral species of 1 does exist in the *N*-hydroxy form as shown. The basic $pK_a$ (1.79) of 1 was found to be similar to that of 2-hydroxypurine (1.69), which indicates that the addition of the 3-hydroxy function to 2-hydroxypurine has little effect on the protonation. The 3-hydroxy-2,3-dihydro-2-oxopurine is very insoluble in water and purification was achieved only by reprecipitation. Unlike 2-hydroxypurine,[13] which ring opens to 4,5-diaminopurine even in pH 5 solution, 1 undergoes ring opening slowly only in strong acid solution at room temperature (in 3 *N* HCl $t_{1/2}$ = 4 days). Like 3-hydroxyxanthine, 1 reacted with acetic anhydride to form the acetyl ester of 1 but the isolation of ester in pure form was not successful owing to its ready hydrolysis. When the freshly prepared acetyl ester was boiled with ethanol, it did not give any 8-ethoxy-2-hydroxypurine; instead a small amount of 2,8-dihydroxypurine[10] (2,3,7,8-tetrahydro-2,8-dioxopurine, 3) and unreacted 1 were obtained. Similar treatment of the acetoxypurine with pH 7.00 buffer also gave a small amount of 3. Reaction of 1 with tosyl chloride in pyridine at room temperature for a prolonged period of time gave some 3, but upon refluxing in pyridine most of the 1 decomposed to non-uv absorbing material and no 3 was detectable. The acetyl ester of 1 prepared in situ by the addition of acetic anhydride to an aqueous solution of 1 with methionine present gave almost a quantitative amount of 2-hydroxy-