solid. Sublimation afforded 100 mg (32%) of colorless solid, mp 209.5–217°. The mass spectrum displayed a parent ion of 156 and other fragmentation ions indicative of a mixture of borneol and isoborneol-2,10-d_2.

When this same reaction was carried out on 10-camphorsulfonyl chloride, only using lithium aluminum *hydride* as the reducing agent, a 47% yield of sublimed, colorless solid was obtained. Analysis by vpc, using a 150-ft capillary poly(propylene glycol) UC oil LB 550-X column, proved that the solid was a 2:1 mixture of isoborneol and borneol, respectively, by comparing retention times with authentic samples.

Camphor-10-d_1.—To a solution of 85 mg (0.54 mmole) of a mixture of borneol and isoborneol-2,10-d_2 in acetone was added 0.2 ml of 8 N CrO_3 in sulfuric acid–water. After standing for a few minutes, the solvent was decanted from the chromium salts and diluted with water. The aqueous acetone solution was extracted with ethyl ether, which, in turn, was washed with water, dried, and evaporated to give a colorless solid. Except for a C–D bond stretch absorption at 4.55 μ, the infrared spectrum (Nujol mull) resembled that of camphor. The sublimed ketone was free of impurities as shown by vpc analysis and was shown to be a monodeuterated camphor by its molecular weight of 153 (mass spectrometry).

Isoborneol-10-d_1.—A mixture of 60 mg of camphor-10-d_1 and 100 mg of lithium aluminum hydride in anhydrous ether was stirred at room temperature for 3 hr. After quenching with aqueous sodium sulfate solution, the aluminum salts were filtered and washed with fresh ether. The filtrate was dried with magnesium sulfate and evaporated. The residue was sublimed to give a colorless solid, mp 207.5–210°, whose infrared spectrum (Nujol mull) resembled that of isoborneol's except for a C–D stretch at 4.55 μ.[24] Its mass spectrum showed a parent ion of 155.

Isoborneol-8,8-d_2.—A mixture of about 18 mg of camphor-8,8-d_2 and a small amount of lithium aluminum hydride in anhydrous ether was stirred at room temperature overnight. After the addition of water, the salts were filtered and washed with fresh ether several times. The ether washings were dried with magnesium sulfate and concentrated in a sublimer. Sublimation gave about 10 mg of colorless solid, mp 205–208°. An infrared spectrum (CCl_4 solution) showed hydroxyl (2.8, 2.9) and C–D stretch (4.5–4.7), but no carbonyl or *gem*-dimethyl absorptions. The mass spectrum showed a parent ion of mass 156 (two deuteriums) and other ions characteristic of an isoborneol derivative.

8-Bromocamphor-8,8-d_2.—Following a procedure described by Sommer,[25] 130 mg (0.77 mmole) of 8-hydroxycamphor-8,8-d_2,[11] 130 mg (1.0 mmole) of quinoline, 220 mg (0.81 mmole) of phosphorus tribromide in 2 ml of bromobenzene were stirred and refluxed at 180° for 1 day. Work-up gave 104 mg (60%) of an oily solid, which showed a strong carbonyl band and no hydroxyl absorption in its infrared spectrum (Nujol mull). The mass spectrum showed a dual parent peak of m/e 232 and 234.

Camphor-8,8-d_2.—Using a microhydrogenation apparatus, 560 mg of 5% palladium on charcoal in 0.8 ml of water, 0.6 ml of ethanol, and 30 mg (0.56 mmole) of potassium hydroxide were stirred in a hydrogen atmosphere for 3 hr. To this mixture was added 90 mg (0.4 mmole) of 8-bromocamphor-8,8-d_2 in 2.5 ml of ethanol. After stirring for 18 hr, the catalyst was filtered and washed with ether. The ether filtrate was washed with water, dried, and evaporated in a sublimer to give an oily solid. Sublimation afforded a colorless solid (22 mg). Analysis by vpc showed that the product was free of impurities and had a retention time identical with that of camphor. Its mass spectrum displayed a parent ion of mass 154 (two deuteriums).

Acknowledgment.—We wish to thank Dr. F. W. McLafferty and Mr. T. Wachs for making it possible to obtain the mass spectra. We are also indebted to Dr. W. Meyer and Dr. A. Lobo for their generous gift of 8- and 9-deuterio-substituted compounds.

(24) The purity of all the deuterated isoborneol derivatives was checked by vpc using a 150-ft capillary poly UC oil column. The only impurities present were the corresponding borneol derivatives.

(25) L. H. Sommer, H. D. Blackman, and P. C. Miller, *J. Am. Chem. Soc.*, **76**, 803 (1954).

Low-Temperature Fluorination of Schiff Bases[1]

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Controlled addition of elemental fluorine to the carbon–nitrogen double bond of benzilidenealkylamines provides a synthetic route to α,α-difluoro secondary fluoramines. Some properties and reactions of these fluoramines are discussed.

It has been demonstrated that the addition of elemental fluorine to complex and reactive organic substrates, such as olefins,[2,3] may be controlled. The process utilizes a combination of low temperatures and inert diluents and provides a convenient synthetic method for vicinal difluorides. The extension of such a process to the carbon–nitrogen double bond, which produces secondary fluoramines, is reported here.

The addition of fluorine to carbon–nitrogen unsaturation has received scant attention and has centered mostly upon the nitrile group. One example is acetonitrile which may be fluorinated with mercuric fluoride at 150 to 180° to produce a host of N-fluoramines, difluoramines, and generally rearranged and variously substituted products.[4] Direct fluorination with elemental fluorine is usually[4] quite destructive and causes extensive cleavage and substitution of the attached organic moiety. Relatively simple substrates had to be used to reduce the number of possible side products.

The method employed successfully[2,3] for the fluorination of olefins was used without modification on the Schiff bases and produced primarily α,α-difluoro secondary fluoramines (I). The additions were conducted at −78° with the substrate as a 10% solution in Freon 11 (CCl_3F). Pure, undiluted fluorine was metered to the solution in such a manner that the partial pressure never exceeded 50 mm. Care must be taken as the reaction can easily become quite violent even at −78°. An inorganic HF scavenger was usually included, and sodium fluoride was found to be marginally effective. Compounds more basic than NaF will react with fluorine or dehydrofluorinate the product.

A number of equivalents of fluorine admitted to the reactor were controlled from pressure-drop measurements. This fluorine/substrate ratio will determine

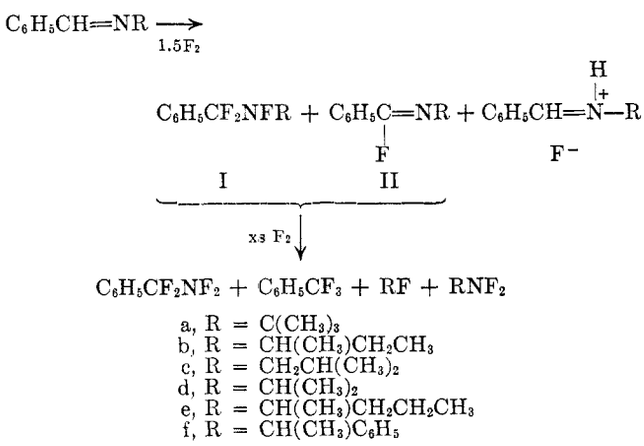
(1) This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract No. DA-01-021 AMC-11536.

(2) R. F. Merritt and T. E. Stevens, *J. Am. Chem. Soc.*, **88**, 1822 (1966).

(3) R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, **31**, 1859 (1966).

(4) For a general review of this area, see M. Hudlicky, "Chemistry of Organic Fluorine Compounds," The MacMillan Co., New York, N. Y., 1962, p 71, and references therein.

the ultimate products. The optimum yield of fluoramine I occurs with F_2/substrate ratios of 1.5/1.0. Increasing the relative amount of fluorine will cause cleavage of C–N bond in the two possible ways, and lead to the formation of alkyl fluorides and alkyl difluoramines. A by-product found in each case was an unstable material of the structure II as shown.

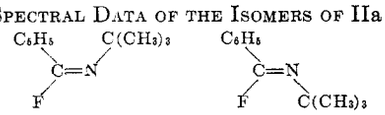


a, R = $C(CH_3)_3$
b, R = $CH(CH_3)CH_2CH_3$
c, R = $CH_2CH(CH_3)_2$
d, R = $CH(CH_3)_2$
e, R = $CH(CH_3)CH_2CH_2CH_3$
f, R = $CH(CH_3)C_6H_5$

The nature of the alkyl groups was varied to provide insight to the fate of the proton(s) adjacent to the nitrogen atom. In no case did side-chain fluorination occur except that caused by C–N bond rupture in the presence of excess fluorine.

Benzilidene-*t*-butylamine was extremely reactive to fluorine at −78° and afforded a crude mixture of Ia and IIa of which the latter decomposed quickly (<5 min) at room temperature. Rapid (<10 min) elution chromatography on silica gel at 10° was necessary for the purification of Ia. The fluoride (IIa) assigned the *anti* configuration (configuration assignments refer to the phenyl and alkyl groups) could not be isolated, but its structure could be inferred from spectra of the crude mixture of it and fluoramine Ia (*cf.* Table I).

TABLE I
SPECTRAL DATA OF THE ISOMERS OF IIa

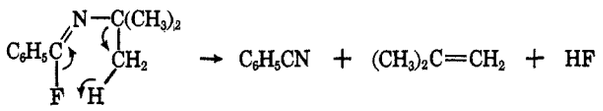


	syn IIa	*anti* IIa
$\nu_{CF=N}$, cm^{-1}	1686	1718
ϕ[a]	+67.0 (singlet)	+39.0 (singlet)
δ[b]	1.50 (doublet, J = 1 cps)	1.40 (singlet)

[a] ϕ = parts per million from internal CCl_3F. [b] δ = parts per million from internal TMS (10% solutions in $CDCl_3$).

The fluoramine Ia is quite stable when pure, but will be quantitatively defluorinated overnight when exposed to glass or silica gel to another compound with spectral characteristics similar to *anti* IIa. On the basis of the following spectral and chemical evidence it is assigned as *syn* IIa. Table I details the various spectral data for the two isomers.

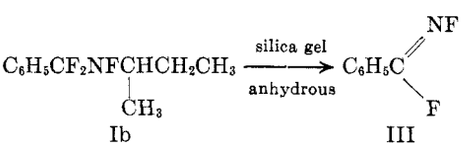
The isomer assigned as *anti* IIa will decompose rapidly at 25° to benzonitrile, isobutylene, *t*-butyl fluoride, and presumably, HF. *syn* IIa is more stable and will not decompose at room temperature. It is expected[5] that the *anti* isomer will present a conformation more conducive to the formation of a cyclic, six-membered transition state for isobutylene, etc., elimination. Such a cyclic process would obviously be less favorable for the *syn* isomer and it would thus be less temperature sensitive.



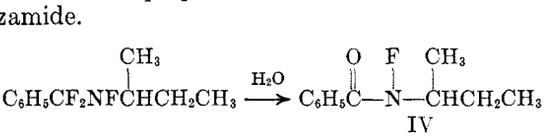
Both isomers may be hydrolyzed to *t*-butylbenzamide so easily that exposure to moist air for 1 hr is sufficient for complete conversion. The analogous chloro compounds prepared by Ugi, Beck, and Fetzer[7] have been shown to hydrolyze easily to the corresponding N-alkyl benzamides.

Additional corroborative information is provided by the small J_{HF} coupling of the *t*-butyl protons observed in the *syn* isomer where the *t*-butyl group and fluorine atom are *trans*. The trend in magnitude of such coupling constants should be $J_{trans} > J_{cis}$.[6]

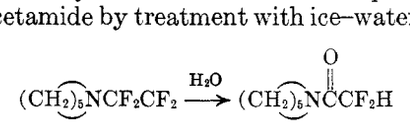
The fluoramines (I) may be rapidly decomposed or degraded by a variety of reagents, the mildest being silica gel. The elution purification will be successful only if normal, untreated hydrated silica ge lis used. If the silica gel is dried by heating under vacuum at ~160° the fluoramine I will not survive the elution, but will be converted to the N-fluorimine (III). This compound is quite stable and the conversion is high enough (~25%) to provide a synthetic method of preparation.



Acid- or base-washed silica gel will cause partial to total hydrolysis of Ib to N-fluoro-N-*sec*-butylbenzamide (IV). The conversion is higher and procedure simpler by dissolving Ib in aqueous methanolic HCl and stirring at 25° for 1 hr. This is also a convenient synthetic procedure for N-fluoro-N-alkylbenzamides. The direct fluorination procedures have not been successful for the preparation of IV from N-*sec*-butylbenzamide.



Hydrolyses of difluoromethylene groups activated by a geminal nitrogen atom have been observed by Raksha and Popov.[8] The tetrafluoroethylene adduct of piperidine is smoothly converted to the corresponding α,α-difluoroacetamide by treatment with ice–water.

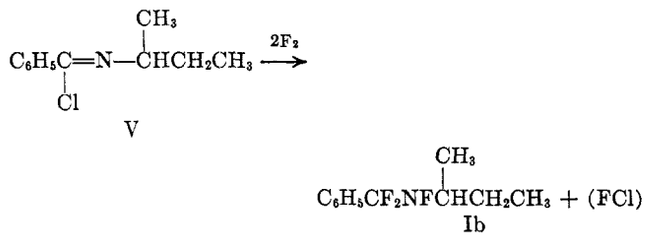


The major factor in the low yield of N-fluoramine (Ia–f) is that the HF by-product is scavenged efficiently by unreacted Schiff base. The resulting immonium salt will then become insoluble and not par-

(5) This is apparently the reason for the greater instability of $C_6H_5C(Cl)=NC(CH_3)_3$ relative to analogous imide chlorides with other substituents on the nitrogen atom (*cf.* ref 6).

(6) R. A. Beauder and J. D. Baldeschwieler, *J. Mol. Spectry.*, **9**, 30 (1962).
(7) I. Ugi, F. Beck, and U. Fetzer, *Ber.*, **95**, 126 (1962).
(8) M. H. Raksha and Yu. V. Popov, *Z. Obshch. Khim.*, **34**, 3465 (1964); *Chem. Abstr.*, **62**, 3929*b* (1965).

ticipate further in the fluorination. This problem was eliminated by replacing the offending proton with a chlorine atom. Such a compound (V) was readily prepared from *sec*-butylbenzamide and thionyl chloride.[7]

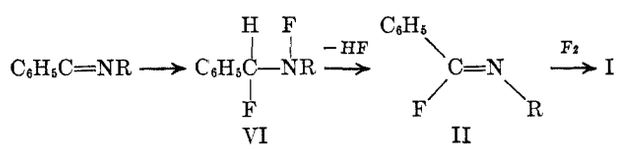


V

Ib

The chloride was more reactive to fluorine than the Schiff base and produced the identical N-fluoramine in considerably higher yield, (63% *vs.* 22%). No chlorine-containing N-fluoramines could be found.

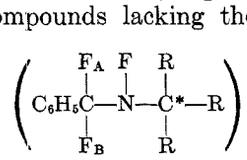
The mechanism of fluorination is probably not significantly different from that postulated for fluorine addition to olefins.[9] An electrophilic addition in which the initial adduct is a difluoride (VI) is as shown.



VI II

A *trans* elimination of HF from the favored conformer of VI would produce the *anti* isomer II. The *anti* II is in fact the only isomer seen in the benzilidine-*t*-butylamine fluorination. Further addition of fluorine to II will result in N-fluoramine I. The HF salt of benzilidine-*t*-butylamine is unreactive to fluorine as would be expected in a primarily electrophilic process. The loss of the chlorine atom is rather unexpected. The benzilic chlorine atom of the initial adduct (C_6H_5-CClFNFR) may probably be easily oxidized and replaced by fluorine in a later step.

The F^{19} nmr spectra of the α,α-difluorofluoramines are unusual in that the fluorine atoms F_A and F_B are magnetically nonequivalent,[10] even though separated by one atom from the optical center, C*. This phenomenon has been observed in other cases[10] with proton spectra but this series of compounds provides the first examples of its generality to fluorine nmr. The chemical shift and coupling constant data for three such compounds are given in Table II, together with data for three similar compounds lacking the optical center.



The F^{19} spectra typically consisted of an AB pattern due to the CF_2 group, in which the lower field pair was further split into doublets by the N-fluorine atom. The N-fluorine resonance was generally at higher field than the CF's and it usually consisted of a four-line multiplet as a result of a large spin–spin splitting by the vicinal proton (confirmed by a collapse upon proton irradiation) and a smaller coupling to the fluorine atom at lower field.

(9) R. F. Merritt, *J. Org. Chem.*, **31**, 3871 (1966).

(10) Similar types of proton nonequivalence have been noted in the cases of benzilic ethers [J. D. Roberts, *et al.*, *J. Am. Chem. Soc.*, **87**, 1058 (1965)], substituted N,N-dimethylbenzylamines [J. C. Randall, Jr., Ph.D. Thesis, Duke University, 1964], and N,N,-dialkylsulfinamides [R. M. Moriarty, *J. Org. Chem.*, **30**, 600 (1965)].

TABLE II

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR $C_6H_5CF_2NFC^*R_3$

Compd	$\phi_{CF_AF_B}$, ppm	ϕ_{NF}, ppm	$J_{F_AF_B}$, cps	J_{F_ANF}, cps	J_{F_BNF}, cps	J_{NFH}[a] cps
Ia	87.3	82.8	...	23	23	...
Ib	83.1, 96.1	109.6	190	19	<1	38
Ic	97.0	73.0	...	13	13	43
Id	90.0	105.2	...	8	8	37
Ie	87.0, 93.0	107.4	191	18	<1	39
If	82.2, 95.4	108.0	192	20	10	31

[a] J_{NFH} refers to the proton(s) geminal to the fluoramino group.

Summary.—It thus appears that direct additions of elemental fluorine to the carbon–nitrogen double bonds are of synthetic utility. This process is probably ionic (electrophilic) and similar to that observed for olefins.[2,3,9]

Experimental Section

Materials.—The fluorine was obtained from Allied Chemical Corp., and was passed through a potassium fluoride HF scrubber before use. The Schiff bases were obtained by refluxing the appropriate amine and aldehyde in benzene with azeotropic removal of the water. The physical properties of the bases agreed with those published previously and the nmr spectra were consistent with the expected structures. All were stored in a nitrogen atmosphere until used.

Procedure.—The general apparatus and detailed operation have been previously described.[3] Care must be taken that the actual addition occurs in the cooled portion of the reactor.

Fluorination of Benzilidene-*t*-butylamine.—The Schiff base (7.0 g, 44 mmoles) was dissolved in 50 ml of Freon 11 (CCl_3F) and 2.0 g of NaF was slurried with the solution. This mixture was cooled to −78° and thoroughly degassed. The fluorine (66 mmoles) was carefully metered to the reactor to keep the pressure below 50 mm. The total reaction time was about 3 hr. The volatile products were removed *in vacuo* at 25° and the crude, unstable residue was immediately placed on a silica gel column (20 × 60 mm). The column was maintained at ~10° by a cooling jacket through which brine was circulated. The difluoro-N-fluoramine (4.3 g, 45% yield) was rapidly eluted with a 20:1 pentane–methylene chloride solvent mixture as a colorless, unstable oil. The remainder of the crude residue consisted of the HF salt of the Schiff base and *anti* IIa.

The infrared spectrum of the fluoramine contained C–F (8.7–9.5 μ) and N–F (10.6 and 11.4 μ) bands and confirmed the absence of functional group absorption from 5.0 to 6.5 μ. The F^{19} nmr spectrum has been described in the discussion and the proton nmr spectrum showed the *t*-butyl group as a doublet (J_{HF} = 2 cps) centered at δ 1.48 and the usual phenyl complex.

Anal. Calcd for $C_{11}H_{14}F_3N$: C, 60.82; H, 6.50. Found: C, 60.47; H, 6.36.

Continued fluorination of the crude product with 7.15 equiv of fluorine produces the four expected cleavage products in varying amounts up to about 40% yield. The four compounds were found in essentially equal amounts and three [$(C_6H_5CF_3$, $(CH_3)_3CNF_2$, and $(CH_3)_3CF$] were identified by comparison of infrared spectra with those of authentic samples.

The fourth product, **α,α-difluorobenzodifluoramine,** was identified by the following spectral properties. Infrared bands for C–F (8.9–9.3 μ) and NF_2 (10.3, 10.51, 10.75, and 11.05 μ) were apparent. The proton nmr contained only aromatic protons, and F^{19} spectrum consisted of a peak at ϕ −17.04 (NF_2) and +103.13 (CF_2). The molecular weight by the mass spectral gaseous effusion method was 179 (theoretical, 179).

Anal. Calcd for $C_7H_5F_4N$: C, 46.94; H, 2.81; N, 7.82. Found: C, 46.16; H, 2.83; N, 7.96.

Decomposition of Fluoramine Ia.—A sample of fluoramine Ia, which had been purified by chromatography was stirred overnight in pentane with silica gel. F^{19} nmr and infrared spectra confirmed the disappearance of Ia and the presence of fluoride *syn* II. When both *syn* II and mixtures containing *anti* II were exposed

to water, they were rapidly converted to *t*-butylbenzamide. The amide was prepared independently and the spectra (infrared and nmr) were identical.

Fluorination of Benzilidene-*sec*-butylamine.—The anil (7.0 g, 44 mmoles) was fluorinated in the manner described above to yield 8.5 g of crude, unstable products. The N-*sec*-butyl analog of *syn* II could be observed in this crude by infrared and nmr. Rapid elution chromatography at 10° (silica gel) produced the fluoramine (Ib, 2.2 g, 22% yield) as a colorless, unstable oil. The fluoramine must be eluted from the column within 10 min or decomposition becomes appreciable. The spectral characteristics are analogous with those of Ia and are included in the discussion section.

Anal. Calcd for $C_{11}H_{14}F_3N$: C, 60.82; H, 6.50; N, 6.45. Found: C, 59.84; H, 6.08; N, 6.29.

Rapid (10 min/10°) elution of the above oil (4.0 g) on anhydrous (150°/0.01 mm/15 hr) silica gel caused elimination of the elements of *sec*-butyl fluoride from Ib with isolation of 1.1 g of a new product, **fluorimine III.** No fluoramine (Ib) could be recovered from the column. Compound III contained bands for C=N (6.05 μ), CF (8.5–9.5 μ), and =NF (10.8 and 11.75 μ) along with the usual monosubstituted phenyl. The proton nmr spectrum contained only aromatic protons, whereas the F^{19} spectrum was two doublets of equal areas centered at ϕ +37.9 (=NF) and +77.9 (=CF) with J_{FF} = 26 cps.[11] The molecular weight determined by the mass spectral effusion method was 133 (theoretical, 141).

Anal. Calcd for $C_7H_5F_2N$: C, 59.57; H, 3.57; N, 9.93. Found: C, 59.55; H, 4.14; N, 9.38.

Hydrolysis of Ib to N-Fluoro-N-*sec*-butylbenzamide (IV).—The fluoramine (1.1 g, 5.1 mmoles) was dissolved in 5.0 ml of methanol containing 1 ml of water and 1 drop of concentrated HCl. The mixture was stirred for 1 hr at 25° and 5 ml of ice-water was added. The insoluble precipitate was extracted with ether; the ether was dried ($MgSO_4$) and stripped to yield 0.6 g (61% yield) of N-fluoro-N-*sec*-butylbenzamide. Attempts at crystallization resulted in decomposition. The infrared (C=O, 5.9–6.05 μ) and proton nmr are in accordance with the postulated structure. The single proton geminal to the NF group appears as a doublet (J_{HF} = 42 cps) of sextets (J_{HH} = 7 cps) centered at δ 4.3. The F^{19} nmr spectrum consists of a doublet (J_{HF} = 42 cps) centered at ϕ +88.9.

Fluorination of Benzilideneisobutylamine.—The anil (3.5 g, 22 mmoles) was fluorinated (33 mmoles, F_2) and chromatographed in the usual manner to afford 0.97 g (21% yield) of the fluoramine Ic. The compound had an infrared spectrum similar to those of the other isomers; the nmr spectrum is included in the discussion section. The adduct would decompose at 25° within 6 hr even when analytically pure, and could not be distilled.

Anal. Calcd for $C_{11}H_{14}F_2N$: C, 60.82; H, 6.50. Found: C, 60.00; H, 6.15.

Fluorination of Additional Anils.—The corresponding α,α-difluoro-N-fluoramines could be prepared when R = 2-pentyl, 1-phenylethyl, and isopropyl. These compounds were too unstable to purify for satisfactory elemental analyses, but the spectral (H^1 and F^{19} nmr) characteristics could be obtained and are included in the discussion section.

Fluorination of Benzilidene-*sec*-butylamine Chloride (V).—The imide chloride was prepared from the corresponding amide *via* the procedure of Ugi, Beck, and Fetzer[7] and was purified by vacuum distillation to a colorless liquid, bp 60–61° (2.5 mm). The imide chloride (4.3 g, 22 mmoles) was fluorinated in the usual manner with 33 mmoles of F_2 to yield 3.0 g (63% yield) of fluoramine Ib *after* chromatography. The spectral properties were identical with those observed of the compound prepared *via* the Schiff base.

(11) R. A. Mitsch, *J. Am. Chem. Soc.*, **87**, 328 (1965). It was noted that in $CFCl_2CF{=}NF$ the =NF appeared at ϕ^* +21.5 and =C—F at +77.2 and the infrared exhibited bands at 5.95 and 11.67 μ (CF=NF).

Acknowledgment.—We are grateful to Mr. Jack Brooks for technical assistance and to Mrs. Carolyn Haney for infrared and nmr spectra.

A New Rearrangement Product in the 6,7-Benzomorphan Series

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6-Methoxy-2,4a,4b-trimethyl-1,2,2a,4b-tetrahydro-1H-indeno[2,1-*c*]pyridine (IIIa) has been identified as the minor product of the thionyl chloride rearrangement of 2′-methoxy-9-hydroxy-2,5,9-trimethyl-6,7-benzomorphan. The structure was assigned by nmr, ultraviolet, infrared, and mass spectral data of IIIa, the hydrogenation product IV, and the Hofmann elimination product (V). The corresponding rearrangement product (IIIb) has been isolated from Ib under identical conditions. Mechanisms for the formation of II, III, and VII from I are proposed. The pyrolysis of 2′-methoxy-9-acetoxy-2,5,9-trimethyl-6,7-benzomorphan perchlorate (VIIIa) afforded VIIa as its only rearrangement product, contrasting with VIIIb which has been reported[2] to give VIIb and IXb.

It was recently reported[2] that the pyrolysis of 9-acetoxy-2,5,9-trimethyl-6,7-benzomorphan perchlorate (VIIIb) gave mixtures of the perchlorates of 1,2,3,4-tetrahydro-1,4,4-trimethyl-9H-indeno[2,1-*b*]pyridine (IXb) and 1,2,4a,9a-tetrahydro-1,4,4a-trimethyl-9H-indeno[2,1-*b*]pyridine (VIIb). Furthermore the corresponding carbinol base of VIII (Ib), in the presence of thionyl chloride, gave the expected methylene derivative (IIb) together with a low yield of the rearrangement product (VIIb).[2,3] Lastly, it has been observed[4] that dehydration of 2′-methoxy-9-hydroxy-2,5,9-trimethyl-6,7-benzomorphan (Ia) by thionyl chloride gave three products, IIa, a monochloro derivative, and an unknown rearrangement product isomeric with IIa. This communication establishes 6-methoxy-2,4a,4b-trimethyl-1,2,4a,4b-tetrahydro-1H-indeno[2,1-*c*]pyridine (IIIa)[5] as the new rearrangement product and completes structural studies on all rearrangement products, detected, so far, in this series. (See Scheme I.)

The high-resolution proton magnetic resonance spectrum of IIIa (Table I) showed four three-proton singlets at 3.85 (OCH_3), 2.63 ($>NCH_3$), and 1.28 and 1.11 ppm (two quaternary CCH_3 resonances). In the olefinic

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(3) H. Kugita and M. Takeda, *Chem. Pharm. Bull.* (Tokyo), **11**, 986 (1963).

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(5) 6-Methoxy-1,2a,2b-trimethyl-1,2,2a,2b-tetrahydro-2H-indeno[2,1-*c*]-pyridine is the IUPAC name for this compound.