The Reaction of Imines with Difluoramine. A Method of Preparation of Diazirines

W. H. Graham

Contribution from Rohm and Haas Company, Redstone Research Laboratories, Huntsville, Alabama 35807. *Received June 24, 1966*

Abstract: Reaction of difluoramine with imines gives a variety of products, the relative ratios of which depend on the structure of the imine. The three type compounds obtained are diazirines, α-haloazo compounds, and α-fluoroalkylidenehydrazines.

The reaction of *t*-octylazomethine with either difluoramine[1] or dichloramine[2] has been shown to give diazirine in practical yields. Presently, we report the reaction of other substituted imines with difluoramine to produce substituted diazirines, α-fluoroazo compounds, or α-fluoroalkylidenehydrazines; the relative yield of these products is a factor of structural features of the starting imine.

Results

The results indicate that formaldehyde imines or negatively substituted aromatic imines yield diazirines in fair yield and as the principal product while imines derived from aliphatic, saturated aldehydes yield a mixture of the corresponding diazirine derivative and α-fluoroazo compound. Imines derived from conjugated aliphatic and aromatic aldehydes yield the corresponding α-fluoroalkylidenehydrazines. These latter products are related to the α-fluoroazo compounds through a simple tautomerization of a mobile hydrogen. If acetic anhydride is used as the reaction medium instead of an inert solvent, the product is a *sym*-acetylacylhydrazine.

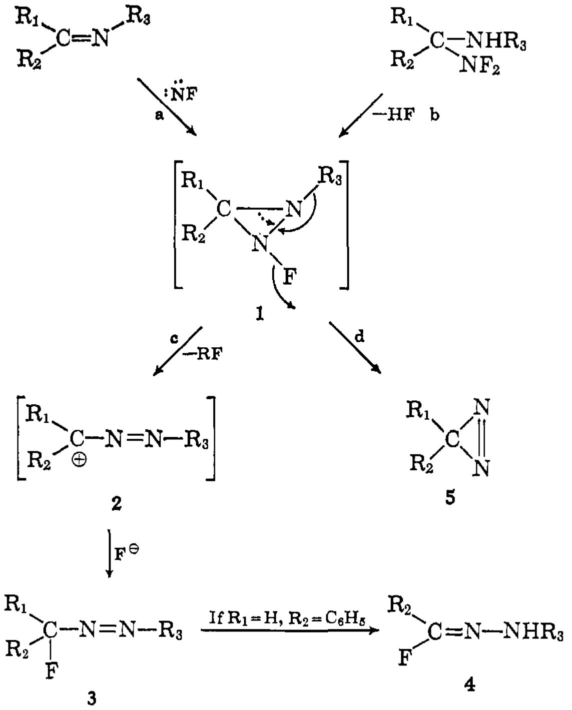
In Table I are listed the principal products identified by reactions of the several imines with difluoramine along with yield and pertinent physical data.

Discussion

Mechanism. The present results can be reasonably accommodated by amplification of the mechanisms proposed for the deamination reactions using difluoramine[3] and the formation of diaziridines using hydroxylamine-O-sulfonic acid.[4] In the former case formation of fluoronitrene by α elimination of the elements of hydrofluoric acid from difluoramine was proposed. Schmitz, on the other hand, presents evidence for a two-step addition–intramolecular S$_N$2 displacement mechanism for diaziridine formation. In the present work it is not possible to distinguish between these two possible mechanisms. By either route, (a) or (b), one would logically arrive at what is believed to be the key intermediate, the N-fluorodiaziridine (1). In the formation of diazirine by the reaction of *t*-octylazomethine and dichloramine pathway b was preferred.[2] However, the reactivity of difluoramine with the present series of substituted imines did not appear to parallel the expected ease of addition to the carbon–nitrogen double bond. Reactions were about equally energetic irrespective of the imine substrate. Such a qualitative relationship would more reasonably parallel the base strength of the imines used.

As pictured in Scheme I, the unstable N-fluorodiazirine can break down in two ways, pathway c and d.

Scheme I



The factor which determines the path of the reaction appears to be the relative ease of carbonium ion formation on the carbon atom of the ring (1 → 2) *vs.* the fragmentation of the group, R$_3$, as a carbonium ion[5] (1 → 5). Reaction by path d to give diazirines predominates when groups R$_1$ and R$_2$ do not stabilize adequately the resulting carbonium ion 2 by resonance or hyperconjugative effects. This factor is especially well illustrated by comparison of the results for the unsubstituted and *p*-nitro aromatic imine. The electron-withdrawing effect of the nitro group greatly decreases the availability of the electrons of the aromatic ring to stabilize an adjacent carbonium ion; the resulting product, *p*-nitrophenyldiazirine, is therefore produced by the alternate route, path d. In contrast, the unsubstituted

---

(1) W. H. Graham, *J. Am. Chem. Soc.*, **84**, 1063 (1962).

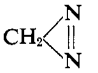
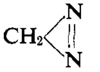
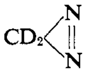
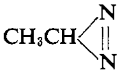
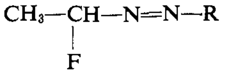
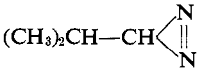
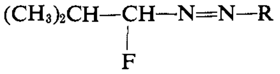
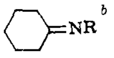
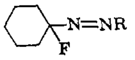
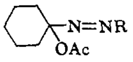
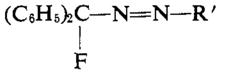
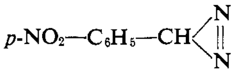
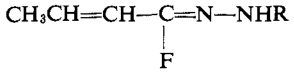
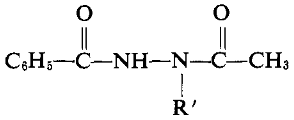
(2) W. H. Graham, *J. Org. Chem.*, 30, 2108 (1965).

(3) C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *J. Am. Chem. Soc.*, **85**, 97 (1963).

(4) E. Schmitz, *Angew. Chem. Intern. Ed. Engl.*, 3, 333 (1964).

(5) A more complete study should include the determination of the effect of replacing R$_3$ by groups other than *t*-butyl and *t*-octyl. In this way the balance of structural features necessary to produce reaction by either path c or d could probably be correlated.

Table I. Reaction of Imines with Difluoramine

Imine[a]	Products	Yield, %	Bp (mm) or mp, °C
$CH_2{=}N{-}R'$		Trace	−14
	Isobutylene		...
	$(CH_3)_3CF$		...
$CH_2{=}NR$		62	−14
	Diisobutylene		...
	t-Octyl fluoride		...
$CHD{=}NR$		...	...
$CD_2{=}NR$		61	...
$CH_3CH{=}N{-}R$		37	...
	 $CH_3-\underset{F}{\underset{\mid}{CH}}-N{=}N-R$	40	48-51 (1.5)
$(CH_3)_2CH{-}CH{=}N{-}R$		...	...
	 $(CH_3)_2CH-\underset{F}{\underset{\mid}{CH}}-N{=}N-R$	...	42 (0.1)
 [b]		70	96 (1)
		62	92 (0.25)
$(C_6H_5)_2C{=}N{-}R'$	 $(C_6H_5)_2\underset{F}{\underset{\mid}{C}}-N{=}N-R'$	67	65[c]
$C_6H_5CH{=}N{-}R'$	$C_6H_5CF{=}N{-}NHR'$	39	60 (1)
$C_6H_5CH{=}N{-}R$	$C_6H_5CF{=}N{-}NHR$	62	100 (1)
$p\text{-}NO_2{-}C_6H_5{-}CH{=}N{-}R'$		83	64-66[c]
$CH_3CH{=}CH{-}CH{=}N{-}R$	 $CH_3CH{=}CH-\underset{F}{\underset{\mid}{C}}{=}N-NHR$	...	...
$C_6H_5CH{=}N{-}R'$[b]	 $C_6H_5-\overset{O}{\overset{\|}{C}}-NH-\underset{R'}{\underset{\mid}{N}}-\overset{O}{\overset{\|}{C}}-CH_3$	47	135-137[c]

[a] R = t-octyl $[(CH_3)_3CCH_2C(CH_3)_2]$, R' = t-butyl. [b] Acetic anhydride used as solvent. Other reactions were generally run in CCl_4 or some other inert solvent. [c] Melting point.

phenyl derivative reacts mainly by path c. Examination of the results in Table I reveals that if both R_1 and R_2 are alkyl groups reaction path c is followed, while if R_1 is hydrogen and R_2 is an alkyl group both path c and path d are significant. If R_2 is unsubstituted aromatic, however, reaction is by path c even if R_1 = H. These results are consistent with carbonium ion stabilizing effects of the substituent groups.[6]

Carbonium ion intermediates adjacent to the azo group have been postulated previously[7] in the reaction of diazonium salts with aliphatic diazo compounds. The tautomeric equilibrium (**3** $\rightleftarrows$ **4**) between azo compounds with α-hydrogen atoms and hydrazones is anticipated.[7,8] Apparently conjugation of the C=N bond with the aromatic ring system promotes formation of **4** in the benzaldehyde imine derivatives at a more rapid rate than the corresponding aliphatic compounds.

Ring opening of the intermediate N-fluorodiaziridine has analogy in the ring opening of haloaziridines[9,10] and halocyclopropanes.[11-14]

The formation of N-acetyl-N'-benzoyl-N-t-butylhydrazine when benzaldehyde t-butylimine was treated with difluoramine in acetic anhydride is rationalized (Scheme II) by formation of N-α-acetoxybenzylidene-

---

(6) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 163.

(7) R. Huisgen and H. J. Koch, *Ann.*, **591**, 200 (1955).

(8) R. O'Connor, *J. Org. Chem.*, **26**, 4375 (1961).

(9) E. K. Fields and J. M. Sandri, *Chem. Ind.* (London), 1216 (1959).

(10) A. G. Cook and E. K. Fields, *J. Org. Chem.*, **27**, 3686 (1962).

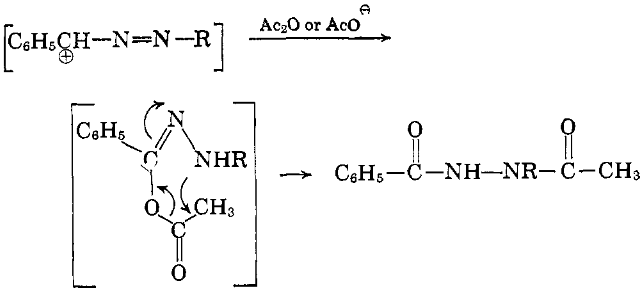
(11) S. M. McElvain and P. L. Wenya, *J. Am. Chem. Soc.*, **81**, 2579 (1959).

(12) W. R. Moore, W. R. Moser, and J. E. LaProde, *J. Org. Chem.*, **28**, 2200 (1963).

(13) R. D. De Selms and C. M. Combs, *ibid.*, **28**, 2206 (1963).

(14) E. Bergman, *ibid.*, **28**, 2210 (1963).

Scheme II



N′-*t*-butylhydrazine followed by an internal acetylation on nitrogen.[15]

Structures. Physical data on diazirine, including mass,[1] infrared,[1,16] ultraviolet,[1,17] and microwave spectra,[18] have amply documented the cyclic structure. In addition the infrared spectra of d_1- and d_2-diazirine have been reported.[16]

The structure of methyl-, isopropyl- and *p*-nitrophenyldiazirine were established by means of their infrared, ultraviolet, and mass spectra. On thermal decomposition the isopropyldiazirine gave nitrogen and isobutylene. This reaction undoubtedly proceeded through a carbene intermediate.[19,20]

The identification of the four α-fluoroazo compounds is based on their F^{19} and H^1 resonance spectra. They decomposed thermally to give nitrogen and upon standing slowly liberated HF.

A single peak at ϕ 138.8 characterized the F^{19} spectrum of the product of the reaction of cyclohexanone *t*-octylimine. The peak was broad with apparent splitting into an unresolved triplet of triplets. This is the pattern expected if the fluorine couples to the dissimilar pairs of adjacent protons. The proton spectrum contained the typical *t*-octyl pattern partially overlapped with the broad cyclohexyl envelope. On the basis of its nmr spectra and decomposition to yield N_2 the product was assigned the structure α-fluorocyclohexylazo-*t*-octane. (See Experimental Section for details of the F^{19} spectrum of α-fluoroethyl-*t*-octyldiimide.)

The product from benzophenone *t*-octylimine was assigned the structure, α-fluorodiphenylmethylazo-*t*-octane, on the basis of its single fluorine peak at ϕ +132.1 and proton spectrum consisting of the *t*-octyl pattern along with the aromatic protons in the expected area ratio, 17:10.

The F^{19} spectrum of α-fluoroisobutyl-*t*-octyldiimide was a doublet (J = 56 cps) of doublets (J = 20) centered at ϕ 163.9. The doublet (J = 56) is due to coupling to the hydrogen on the same carbon as the fluorine while the doublet (J = 20) results from coupling to the proton on the adjacent carbon.

The methine hydrogen on the same carbon as fluorine is a doublet (J = 56) of doublets (J = 5) centered at τ 5.14.

The identification of the product of the reactions of benzaldehyde *t*-butyl- and *t*-octylimines and crotonaldehyde *t*-octylimines as the hydrazine derivatives is based on their characteristic infrared, F^{19}, and H^1 spectra as well as the preparation of stable, crystalline hydrochloride salts which facilitated elemental analyses. Treatment of the hydrochlorides with sodium bicarbonate gave back the original basic hydrazone.

The F^{19} spectrum of N^1-α-fluorobenzylidene-N^2-*t*-butylhydrazine and N^1-α-fluorobenzylidene-N^2-*t*-octylhydrazine consisted of a sharp peak at ϕ +83.7 and +85.2, respectively. The proton nmr pattern of each was that expected of an aromatic compound with an α-sp^2 carbon atom attached to a heteroatom. The *ortho* protons were thus shifted downfield from the *para* and *meta* protons. The N–H proton absorption appeared at τ 5.43 and 4.82 (relative to C_6H_6). The C=N bond infrared absorption is at 1640 cm^{-1}.

The F^{19} spectrum of N^1-α-fluorocrotylidene-N^2-*t*-octylhydrazine is a doublet at ϕ 84.1 (J = 23 cps). The coupling is apparently to the adjacent vinyl hydrogen atom.

The structure of the product N-acetyl-N^1-benzoyl-N-*t*-butylhydrazine is based on its proton nmr and infrared spectra. The proton spectrum consisted of peaks at τ 2.15 (*o*-H, 2), 2.63 (*p*- and *m*-H, 3), 8.55 (CH_3, 3), and −0.9 (N–H, 1). The compound absorbed at 1680 (CH_3CON), 1640 (C_6H_5CON), and 1575 cm^{-1} (amide II band).

Experimental Section

Diazirine. Into an evacuated U tube equipped with a stirring bar and manometer (total volume 250 ml) and containing a solution of 1.41 g (0.01 mole) of *t*-octylazomethine[21] in 5 cc of CCl_4 was condensed 224 ml (0.01 mole) of difluoramine[22] by means of a −130° slush bath. This bath was replaced by an ice bath and the solution was stirred. After an initial pressure decrease (probably HNF_2 uptake) the pressure increased to a steady value of 360 mm after 2–3 hr. The contents were then fractionated by means of a bulb-to-bulb fractionation through a series of three traps at −80, −126 (methylcyclohexane), and −196°. The diazirine was held up mainly in the −126° trap although some reached the −196° trap. It was subsequently found that a −142° trap (methylcyclopentane) would hold up nearly all the diazirine. The yield was 140 cc (62%) of the product which was contaminated only by traces of N_2O and CO_2. Diisobutylene was held up in the −80° trap. The residue contained bifluoride salts as indicated by infrared. Apparently the greater than stoichiometric yield (*i.e*,, 50%) was accounted for by the fluoride ion which acted as a base on difluoramine. (See ref 1 for infrared, ultraviolet, and mass spectra of diazirine.) The proton resonance spectrum was a single peak at τ 9.15.

d_1- and d_2-Diazirine. The method used was similar to that used for the preparation of diazirine. The deuterated *t*-octylazomethine derivatives were prepared from formaldehyde-d_1 and -d_2.[23] The infrared spectra of both compounds are reported and analyzed in ref 16.

Reaction of Acetaldehyde *t*-Octylimine and Difluoramine. Above an evacuated solution of 4.65 g (0.03 mole) of acetaldehyde *t*-octylimine dissolved in 30 ml of CCl_4 at 0°, 224 ml (0.01 mole) of difluoramine was allowed to expand slowly from a small side tube. The mixture was stirred by means of a magnetic stirrer for 2.5 hr at 0° and for 20 min at 20°. The volatile contents were removed under vacuum through a train of four cold traps at −80, −110, −126, and −196°. The volatile contents of the −110 and −126° were combined and analyzed by mass spectral, infrared, and ultraviolet spectra. The infrared spectrum was characterized by the N=N stretch at 1580 cm^{-1} and the C–N stretch at 972 cm^{-1}. The ultraviolet spectrum had the fine structure characteristic of diazirines[1] but was shifted

---

(15) J. T. Edward and S. Samad, *Can. J. Chem.*, **41**, 1638 (1963).

(16) R. Ettinger, *J. Chem. Phys.*, 40, 1693 (1964).

(17) J. A. Merritt, *Can. J. Phy.*, 40, 1683 (1962).

(18) L. Pierce and Sr. V. Dobyns, *J. Am. Chem. Soc.*, **84**, 2651 (1962).

(19) H. M. Frey and I. D. R. Stevens, *ibid.*, **84**, 2647 (1962).

(20) E. Schmitz, D. Habish, and A. Stark, *Angew. Chem. Intern. Ed. Engl.*, **2**, 548 (1963).

(21) M. D. Hurwitz, U. S. Patent 2,582,128 (1952).

(22) W. H. Graham and C. O. Parker, *J. Org. Chem.*, **28**, 850 (1960), and references cited therein.

(23) Supplied by Merck Sharp and Dohme of Canada, Ltd., Montreal, Canada, as paraformaldehyde.

to longer wavelength than the parent diazirine. The strongest absorption was at 344 mμ (ϵ 199). The more prominent mass peaks and their relative intensity are 12 (6.7), 13 (14.6), 14 (17.4), 15 (18.3), 24 (6.5), 25 (10.4), 26 (66.0), 27 (58.9), 27.5 (1.8), 28 (100.0), 38 (2.1), 39 (2.1), 40 (3.1), 41 (11.8), 55 (0.4).

The yield of methyldiazirine was 61 cc (STP), 27% of theory based on difluoramine.

The residue in the reaction flask was poured into 10% HCl and extracted several times with CH_2Cl_2. The extract was washed several times with water and dried, and the solvent was stripped off. The weight of crude residue was 1.75 g. Distillation through a Holzman column yielded 0.52 g of pale yellow liquid, bp 48–51° (1.5 mm). The identity of the product was established as α-fluoroethyl-*t*-octyldiimide by its proton and fluorine resonance spectra and its ultraviolet and infrared spectrum.

The proton spectrum consisted of the typical *t*-octyl pattern at τ 8.16, 8.83, and 9.11 in the area ratio 2:6:9. The methyl adjacent to the fluorine and methine hydrogen coupled to both and was a doublet (J = 22 cps) of doublets (J = 6 cps) centered at τ 8.62. The methine hydrogen, being coupled to the α-fluorine (J = 56 cps) and the adjacent methyl hydrogens (J = 6 cps), is a doublet of quartets centered at τ 4.78.

The F^{19} spectrum was a doublet (J = 56 cps) of quartets (J = 22 cps) centered at ϕ +155.7. Heterodecoupling of the fluorine by irradiation of the methyl proton gave a clean doublet from residual coupling to the methine hydrogen. Irradiation of the methine hydrogen collapsed the F^{19} spectrum to a quartet. Heterodecoupling of the methyl proton collapsed the doublet of doublets to a doublet, the high-field portion of which was obscured by the *t*-octyl protons. The methine proton spectrum was collapsed to a quartet.

The ultraviolet spectrum consisted of two broad absorption bands at 274 (ϵ 58) and 365 mμ (ϵ 21). These values are compatible with those reported.[24] *Anal.* Calcd for $C_{10}H_{21}N_2F$: C, 63.9; H, 11.17; N, 14.9. Found: C, 63.24; H, 11.39; N, 15.75.

The yield of α-fluoroethyl-*t*-octyldiimide based on comparison of the proton spectrum of the crude and distilled product is estimated at 56% based on difluoramine. The ratio of diimide to methyldiazirine is thus approximately 2:1.

The experiment was repeated using 0.03 mole of acetaldehyde *t*-octylimine and 0.026 mole of HNF_2. The yield of methyldiazirine was 37% and of diimide approximately 40%.

Reaction of Cyclohexanone *t*-Octylimine and Difluoramine. Preparation of α-Fluorocyclohexyl-*t*-octyldiimide. Into an evacuated 1-l. round-bottomed flask surrounded by an ice bath and containing 4.18 g (0.02 mole) of cyclohexanone *t*-octylimine dissolved in 50 ml of CCl_4 was expanded 607 cc (0.027 mole) of difluoramine while the solution was stirred by means of a magnetic stirring bar. The mixture was stirred for 1 hr at 0° and 1.5 hr at ambient temperature. The volatile contents were removed by pulling under vacuum through U tube traps at −80, −110, and −196°. Mass spectral and infrared analyses of the contents of these traps revealed only the presence of recovered difluoramine and CCl_4.

The residue was taken up in CH_2Cl_2, shaken with 5% aqueous HCl and water, and then dried. The solvent was removed under vacuum and 4.25 g of liquid residue was obtained. The proton and F^{19} nmr spectra indicated the product was at least 80% α-fluorocyclohexyl-*t*-octyldiimide, 70% yield based on imine. The spectra compared with those obtained on fractions obtained after chromatography through silica gel. There was some decomposition during chromatography.

The identity of the product is based on its F^{19} and H^1 resonance spectra and ultraviolet and infrared spectra and comparison with the corresponding spectra from the related α-acetoxycyclohexyl-*t*-octyldiimide and α-acetoxycyclohexylmethyldiimide, the latter being prepared by an independent method.

The F^{19} resonance spectrum was a single broad, structured peak centered at ϕ 138.8. The peak can be interpreted as a triplet of triplets with J approximately 30 and 10 cps. This can be interpreted as different coupling of the adjacent axial and equatorial hydrogens.

The proton spectrum consisted of the typical sharp *t*-octyl pattern at τ 9.10, 8.65, and 8.15 in the relative area of 9:6:2. The cyclohexyl protons were a broad, structureless pattern with a maximum at τ 8.29.

The compound absorbed in a broad symmetrical band centered at λ_{max} 365 mμ (ϵ_{max} 13). This compare swell with the α-acetoxycyclohexylmethyldiimide, λ_{max} 357.5 (ϵ_{max} 24.1).

Attempted chromatography through silica gel resulted in decomposition although a fraction was collected which had the same physical properties as the crude product. This sample was submitted for elemental analyses. *Anal.* Calcd for $C_{14}H_{27}N_2F$: C, 69.37; H, 11.23; N, 11.56; F, 7.84. Found: C, 68.29; H, 11.09; N, 11.36; F, 9.85.

Reaction of Cyclohexanone *t*-Octylimine with Difluoramine in Acetic Anhydride. Preparation of α-Acetoxycyclohexyl-*t*-octyldiimide. Into an evacuated 100-ml round-bottomed flask containing 35 ml of acetic anhydride and surrounded by an ice bath, to which had been added 4.18 g (0.02 mole) of cyclohexanone *t*-octylimine immediately before, was allowed to expand 500 cc (0.022 mole) of HNF_2. The solution warmed rapidly to 25° but after 10 min the temperature began to drop. The solution was stirred overnight at ambient temperature.

The volatile contents were removed under vacuum through a train of U tubes at −80, −126, and −196°. The −80° trap contained a large amount of acetyl fluoride as indicated by the mass spectrum of the vapor.

The liquid remaining in the reaction flask was diluted with CH_2Cl_2 and washed with 5% $NaHCO_3$ with cooling. The layers separated and, after washing the CH_2Cl_2 again with water, the solution was dried over $CaCl_2$. The solution was filtered and volatile contents were removed on a rotary evaporator, then on a vacuum line for 3 hr. The dark brown residue, 4.32 g, was chromatographed through silica gel and, although there was some apparent decomposition on the column, a fraction, 2.01 g, was obtained to which is assigned the structure α-acetoxycyclohexyl-*t*-octyldiimide. Based on comparison of the proton nmr spectrum of the crude and chromatographed fraction the yield is estimated as 3.4 g, 62% based on cyclohexanone *t*-octylimine.

The proton nmr spectrum consisted of the usual *t*-octyl pattern at τ 9.08, 8.88, and 8.18 in the area ratio 9:6:2. The acetoxy methyl was a sharp singlet at τ 6.98 and the cyclohexyl protons were contained in a broad envelope with a maximum at τ 8.40.

The ultraviolet spectrum consisted of a broad symmetrical band at λ_{max} 360 mμ (ϵ_{max} 29.3) and shoulders on the end absorption at 282.5 and 249 mμ. This spectrum compares closely with that obtained on α-acetoxycyclohexylmethyldiimide obtained by an independent synthesis.

The infrared spectum was characterized by the strong C=O absorption at 1745 cm^{-1} and the carbon–oxygen stretch at 1215 cm^{-1}. *Anal.* Calcd for $C_{16}H_{30}N_2O_2$: C, 68.04, H, 10.71; N, 9.92. Found: C, 67.12; H, 10.94; N, 11.55.

Reaction of Benzophenone *t*-Octylimine with Difluoramine. Preparation of (α-Fluorodiphenylmethyl)-*t*-octyldiimide. Into a solution of 2.93 g (0.01 mole) of benzophenone *t*-octylimine dissolved in 25 ml of CCl_4 and contained in an evacuated 100-ml round-bottomed flask was allowed to expand 350 cc (0.015 mole) of HNF_2. The contents were allowed to warm slowly from 0 to 25° over a period of 2 hr at which time the volatile contents were removed under vacuum through a train of U tube traps at −80, −126, and −196°. The reaction residue was taken up in CCl_4, washed briefly with 10% HCl and water, and dried over $CaCl_2$. The solvent was removed on a rotary evaporator and then the contents were pumped on for 2 hr on the vacuum line. The thick liquid residue crystallized upon cooling briefly and scratching with a glass rod. The yield of crude product of estimated 95% purity was 2.15 g, 67% of theory based on imine. The solid, upon crystallization from MeOH, melted at 65° and decomposed upon pyrolysis in an evacuated mass spectral bulb to liberate nitrogen.

The proton spectrum was the usual *t*-octyl pattern with sharp singlet peaks at τ 9.25, 8.79, and 8.15 in the ratio of 9:6:2. The aromatic protons were split into the 3:2 pattern in the range τ 2.20–3.00. The F^{19} spectrum was a singlet at ϕ +132.1. *Anal.* Calcd for $C_{21}H_{27}N_2F$: C, 76.6; H, 8.55; N, 8.87; F, 6.02. Found: C, 77.30; H, 8.56; N, 8.44; F, 5.66.

Reaction of *p*-Nitrobenzaldehyde *t*-Butylimine with Difluoramine. Preparation of *p*-Nitrophenyldiazirine. Into a solution of 1.03 g (0.005 mole) of *p*-nitrobenzaldehyde-*t*-butylimine dissolved in 15 ml of CCl_4 and contained in a 100-ml round-bottomed flask was expanded 224 cc (0.01 mole) of HNF_2. The solution was stirred for 2 hr at ambient temperature and the volatile contents were removed under vacuum through a train of U tube traps at −80, −126, and −196°. To the residue in the reaction flask was added 25 ml of CH_2Cl_2, and the solution was washed with 10% HCl solution, then water, and dried over $CaCl_2$. The solution was filtered and solvent stripped off to yield a yellow solid, 0.67 g, 83% of theory, identified as *p*-nitro-phenyldiazirine. The solid upon recrystallization from methanol–pentane was obtained as yellow needles, mp 67–67.5°.

---

(24) L. Spialter, D. H. O'Brien, G. L. Untereiner, and W. A. Rush, *J. Org. Chem.*, 30, 3278 (1965).

Prominent in the infrared spectrum was the strong N=N stretch typical of diazirines at 1575 cm^{-1}. The ultraviolet spectrum consisted of a shoulder at λ 342 mμ (ε 1710) as well as the aromatic ring absorptions at λ_{max} 224 mμ (ϵ_{max} 11,300) and λ_{max} 217 mμ (ϵ_{max} 9710). The proton spectrum showed only the diazirine proton as a singlet at τ 7.87 and the A_2B_2 quartet similar in shape and position to that of *p*-chloronitrobenzene.

The sensitivity on the drop-weight tester was 50% fires at 2 in. (RDX = 10 in.). *Anal.* Calcd for $C_7H_5N_3O_2$: C, 51.50; H, 3.67; N, 25.8. Found: C, 51.26; H, 3.41; N, 25.63.

Reaction of Benzaldehyde *t*-Octylimine and Difluoramine. Preparation of N^1-α-Fluorobenzylidine-N^2-*t*-octylhydrazine. Into a stirred solution of 4.34 g (0.02 mole) of benzaldehyde *t*-octylimine in 25 ml of CCl_4 contained in a 110-ml evacuated U tube was admitted 448 ml (0.02 mole) of HNF_2. The solution was stirred at 0° for 30 min and then allowed to warm to room temperature for an additional 30 min.

The volatile contents were removed by pumping briefly through cold traps at −80, −126, and −196°. The remainder of the CCl_4 solution was shaken briefly with 10 ml of H_2O and the layers were separated. An aliquot of the CCl_4 solution was evaporated to the nonvolatile residue and physical measurements were obtained on the product, identified as N^1-α-fluorobenzylidene-N^2-*t*-octylhydrazine.

The F^{19} spectrum was a sharp singlet at φ +85.2. The proton spectrum consisted of the typical *t*-octyl pattern at τ 9.10, 8.83, and 8.55 in the area ratio 9:6:2. The N–H resonance was observed as a broad band centered at τ 4.82. The aromatic protons were split into the typical aromatic 3:2 pattern at τ 3.00 and 2.50.

The approximate boiling point was 100° (1 mm). To the bulk of the CCl_4 solution was added dropwise 3 ml of concentrated HCl. A white solid formed immediately, filtered off, and washed with anhydrous ether. The yield of dried product was 3.55 g, 62% of theory, of N^1-α-fluorobenzylidene-N^2-*t*-octylhydrazinium hydrochloride. The sample sublimed, mp 115° dec. The F^{19} spectrum was a sharp singlet at φ +42.0. *Anal.* Calcd for $C_{15}H_{24}N_2ClF$: C, 62.90; H, 8.40; N, 9.78; F, 6.64; Cl, 12.40. Found: C, 62.55; H, 9.00; N, 9.75; F, 6.30; Cl, 11.70.

Reaction of Benzaldehyde *t*-Butylimine and Difluoramine in Acetic Anhydride. Preparation of N-Acetyl-N^1-benzoyl-N-*t*-butylhydrazine. Into a solution of 1.61 g (0.01 mole) of benzaldehyde *t*-butylimine dissolved in 10 ml of acetic anhydride was allowed to expand 300 cc of HNF_2. The reaction was stirred at ambient temperature for 2 hr. The volatile contents were removed under vacuum until a solid residue remained. The residue was washed with 30 ml of cold ether. From the 1.1 g (47% of theory) of white solid residue was obtained 0.8 g of crystalline material, mp 135–137°.

The infrared spectrum was characterized by absorption at 3300 cm^{-1} (amide N–H), at 1675 cm^{-1} (acetyl carbonyl, CH_3CON), and at 1640 cm^{-1} (benzoyl carbonyl, C_6H_5CON.) The infrared evidence points to the formation of N-acetyl-N^1-benzoyl-N-*t*-butylhydrazine rather than the unrearranged acetoxybenzylidene hydrazone because the ester acetoxy group should absorb at a higher wavenumber.

The proton nmr spectrum, run in $CDCl_3$, consisted of a sharp single peak at τ 8.55 due to the methyl group adjacent to the carbonyl and the aromatic 3:2 pattern at τ 2.63 and 2.15. The single amide proton was observed at τ −0.9. *Anal.* Calcd for $C_{13}H_{18}N_2O_2$: C, 66.67; H, 7.69; N, 11.90. Found: C, 66.73; H, 7.90; N, 11.89.

Acknowledgment. This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Alabama, under Contract Number DA-01-021 AMC-11536(Z).

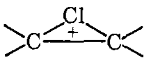
Polar Additions to Olefins. II. The Chlorination of Di-*t*-butylethylene[1]

Robert C. Fahey

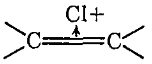
Contribution from the Department of Chemistry, University of California, San Diego, La Jolla, California 92038. *Received May 25, 1966*

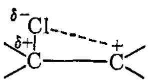
Abstract: The polar chlorination of *cis*-di-*t*-butylethylene in carbon tetrachloride gives *dl*-3,4-dichloro-2,2,5,5-tetramethylhexane (**3**) without concurrent formation of rearranged products. Chlorination of *trans*-di-*t*-butylethylene leads to *meso*-3,4-dichloro-2,2,5,5-tetramethylhexane (**4**) along with the rearranged product (**5b**) resulting from a stereospecific shift of a methyl group. These results show that both dichloride formation and rearrangement occur directly from a bridged chloronium ion. The *trans* stereospecificity of addition (>99.5%) to the *cis*-olefin, which is destabilized relative to the *trans* isomer by 9.3 kcal, indicates that substantial stabilization toward rotational isomerism is present in the intermediate chloronium ion as a result of the chlorine bridging.

The formation of chlorine-bridged cations or chloronium ions (**1**) is a marginal phenomenon as is shown by the nonstereospecific addition of chlorine to arylalkenes[2] as compared with stereospecific *trans* addition to symmetrical dialkyl olefins.[3] The lack of significant rate acceleration by a neighboring chlorine atom in solvolysis reactions[4] has been taken as evidence that the driving force for the formation of chlorine-bridged ions is small. In view of this weak driving force for chlorine bridging, two questions are of interest with respect to the intermediate formed in the chlorination of linear alkenes. First, is the cation a symmetrically bridged chloronium ion (**1**)[5] or does it have an unsymmetrical structure (**2**) of the type considered by de la Mare[6] in which electrostatic interactions between the carbonium carbon and the chlorine atom prevent


1a

or


1b


2

---

[1] Supported by National Science Foundation Grants GP-2647 and GP-5852.

[2] R. C. Fahey and C. Schubert, *J. Am. Chem. Soc.*, **87**, 5172 (1965), and references therein.

[3] (a) H. J. Lucas and C. W. Gould, *ibid.*, **63**, 2541 (1941); (b) M. L. Poutsma, *ibid.*, **87**, 2161 (1965); (c) M. L. Poutsma, *ibid.*, **87**, 2172 (1965).

[4] E. Grunwald, *ibid.*, **73**, 5458 (1951); S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

[5] The alternative formulation for the chloronium ion (**1a**) as a π-complex (**1b**) has been proposed by Dewar: M. J. S. Dewar, *Bull. Soc. Chim. France*, **18**, C71 (1951).

[6] P. B. D. de la Mare in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 93–95.