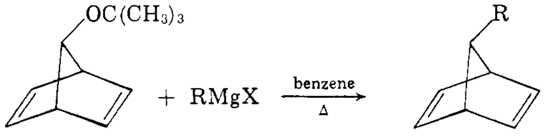
their 1 and 2 isomers and at best give a mixture of isomeric products even when generated *in situ*.[2]

7-*t*-Butoxynorbornadiene, prepared by treating norbornadiene with *t*-butyl perbenzoate, has recently proven to be a valuable precursor for the synthesis of several other 7-substituted norbornadienes.[3,4]

We now wish to report the preparation of 7-methyl- and 7-phenylnorbornadiene by treatment of 7-*t*-butoxynorbornadiene with the appropriate Grignard reagent as shown in equation 1.



(1)

I

IIa. R = CH$_3$-
b. R = Ph-

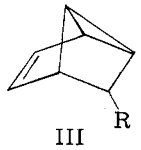
Presumably the reaction could be extended to the synthesis of many alkyl and aryl substituted norbornadienes.

Refluxing the ether (I) with an excess of methylmagnesium iodide in benzene gave a 57% yield of 7-methylnorbornadiene (IIa). Similar treatment of the ether (I) with phenylmagnesium bromide gave 7-phenylnorbornadiene (IIb) in 75% yield. 7-Norbornadienol was not detected among the products; however, it was not rigorously sought. In fact, no other monomeric products were detectable.

The structures of IIa and IIb were established by analysis of their infrared and n.m.r. spectra. Both molecules exhibited the highly characteristic infrared absorptions at 6.5 μ (double bond stretch and at *ca.* 13.6–14.0 μ (*cis* double bond, carbon–hydrogen out-of-plane deformation) indicative of the norbornadiene nucleus.[3] The n.m.r. spectra also were highly characteristic of the norbornadiene nucleus[3] and consistent with the proposed structures. For example, in the 7-methylnorbornadiene spectrum, the methyl group appears as a doublet at $\tau = 9.15$. The bridge hydrogen (7) appears as a complex quartet at $\tau = 7.40$ and the bridgehead hydrogens (1,4) appear as a multiplet at $\tau = 6.82$. In addition, the two pairs of olefinic hydrogens appear as two separate triplets at $\tau = 3.29$ and 3.52 in characteristic fashion.

Several ethers have been cleaved by Grignard reagents to yield analogous hydrocarbons.[5] In most of these examples, at least one moiety was capable of supporting a positive charge. For example, diallyl ether and benzyl ethers are rather easily cleaned to generate hydrocarbons.

The relatively facile cleavage of I is consistent with the stability of the 7-norbornadienyl carbonium ion[4,6] and probably is mechanistically similar to the lithium aluminum hydride reduction of 7-chloronorbornadiene.[7] There is one important exception. The reduction of 7-chloronorbornadiene yielded, in addition to norbornadiene, tricyclo[4.1.0.0^{3,7}]heptene-4 as the major product. The corresponding 2-substituted tricyclo[4.1.0.0^{3,7}]heptene-4 (III) was not observed in the reaction of Grignard reagents with I. However, the tricyclic olefins (III) may have been destroyed under the reaction conditions.



III

Experimental

7-Methylnorbornadiene (IIa).—Following the general procedure of Normant,[8] methylmagnesium iodide was prepared from 57.6 g. (2.4 g.-atoms) of magnesium and 341 g. (2.4 moles) of methyl iodide in 1.5 l. of anhydrous ether. About 1 to 1.5 l. of reagent grade benzene was added in several portions while the ether was removed by distillation. Distillation was continued until the boiling point reached 79°. After the solution was allowed to cool 10–20°, 200 g. (1.22 moles) of 7-*t*-butoxynorbornadiene (I)[3] was added all at once. This mixture was stirred and refluxed for 2.5–3 days. After this time, the excess Grignard was destroyed with about 225 ml. of water and the benzene solution decanted. The solvent was removed at atmospheric pressure with a 24-in. spinning bond distillation column. The product was distilled on the same column to give 74.5 g. (57.6%) of 7-methylnorbornadiene (IIa), b.p. 54.5–55.0° (113 mm.). Infrared (carbon tetrachloride, μ): 3.4 (s), 6.5 (m), 7.6 (s), 13.9 (s). N.m.r. (carbon tetrachloride, τ): 3.29 (3), 3.52 (3), 6.82 (6), 7.40 (4), 9.15 (2), area ratio of 2:2:2:1:3.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.68; H, 9.43.

7-Phenylnorbornadiene (IIb).—Using the same procedure, 7-phenylnorbornadiene (IIb) was prepared from 14.4 g. (0.6 g.-atom) of magnesium, 94.2 g. (0.6 mole) of phenyl bromide, and 50 g. (0.3 mole) of 7-*t*-butoxynorbornadiene (I) to give 38.9 g. (75.8%) of IIb, b.p. 80–81° (1.7 mm.). This product was about 95% pure. Greater purity was obtained by gas phase chromatography using a 20 ft × 3/8 in. 10% Dow 710 silicone column at 160°. Infrared (neat, μ): 3.2 (m), 6.5 (m), 7.6 (s), 13.5 (m), 13.8 (s), 14.4 (s). N.m.r. (carbon tetrachloride, τ): 2.97 (m), 3.15 (3), 3.5 (m), 6.25 (m), area ratio 5:2:2:3.

Anal. Calcd. for $C_{13}H_{12}$: C, 92.81; H, 7.19. Found: C, 93.07; H, 7.41.

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(2) R. Vanelli, Ph.D. thesis, Harvard University, 1950.

(3) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

(4) P. R. Story and M. Saunders, *J. Am. Chem. Soc.*, **84**, 4876 (1962).

(5) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Chap. XV, Prentice-Hall, New York, N. Y., 1954; C. M. Hill, L. Haynes, D. E. Simmons, and M. E. Hill, *J. Am. Chem. Soc.*, **80**, 3623 (1958).

(6) S. Winstein and C. Ordronneau, *ibid.*, **82**, 2084 (1960).

(7) P. R. Story, *ibid.*, **83**, 3347 (1961).

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Fluorine-Containing Nitrogen Compounds. V. Difluoronitroacetamidines and Difluoronitromethyl-1,2,4-triazoles[1,2]

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Received November 26, 1962

The reaction of ammonia or primary or secondary alkylamines with perfluoroalkylnitriles has been shown to afford good yields of stable perfluoroalkylamidines.[3,4] The stability of the perfluoroalkylamidines, as contrasted with their unfluorinated analogs, was attributed to the electronegativity of the fluorocarbon radical.[4]

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(1) This work was performed under the suspices of the U. S. Atomic Energy Commission.

(2) For paper number IV of this series, see G. C. Shaw, D. L. Seaton, and E. R. Bissell, *J. Org. Chem.*, **26**, 4765 (1961); for paper number III, see E. R. Bissell, *ibid.*, **26**, 5100 (1961).

(3) D. Husted, U. S. Patent 2,676,985 (April, 1954).

(4) W. L. Reilly and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 6032 (1956).

TABLE I

PHYSICAL PROPERTIES AND ANALYSES OF DIFLUORONITROACETAMIDINES AND 3-(DIFLUORONITROMETHYL)-1,2,4-TRIAZOLES

Compound	% Yield[a]	M.p., °C.	d_{25}	$n^{25}D$	% Carbon		% Hydrogen		% Nitrogen	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
Ia	63		1.623	1.4491	17.27	17.10	2.17	1.47		
Ia CF_3COOH salt		173–174 dec.			18.98	19.19	1.59	1.42	16.60	16.87
Ib	63		1.451	1.4425						
Ib Hydrobromide		181–182 dec.			15.40	15.26	2.15	2.52	17.96	18.90
Ic	35	34–36	1.345	1.4388						
Ic Hydrobromide		165–167			19.37	18.68	3.25	2.98	16.94	16.83
Id	65		1.374	1.5268	44.65	44.83	3.28	3.18	19.53	20.18
Id Hydrobromide		174–175			32.45	32.50	2.38	2.59	14.19	13.87
Ie	30[b]	91.5–92.5			38.17	38.04	2.14	2.56	14.84	15.54
IIa	86		1.630	1.4480						
IIa Copper chelate		>200			16.52	16.56	0.35	0.58	24.08	24.47
IIb	63		1.572	1.4511						
IIc	40		1.596	1.4546						
IId	60		1.455	1.5172						
IIIa	50	76–77			21.96	21.83	1.23	1.14	23.16[c]	23.02[c]
IIIb	33		1.694	1.4701	26.97	27.12	2.26	1.65		

[a] Based on difluoronitroacetonitrile charged. [b] 90% based on unrecovered nitrile. [c] Fluorine.

Aromatic amines failed to react, presumably because of their low basicity.[4] The unsubstituted perfluoroalkylamidines decomposed smoothly above their melting points with the evolution of ammonia to form 2,4,6-tris(perfluoroalkyl)-1,3,5-triazines.[5]

The present paper describes the reactions of ammonia and primary and secondary amines with a nitrile in which the electronegativity of the alkyl group is further increased over that of the perfluoro compounds by substitution of a nitro group for one of the fluorines. The effect on the reactivity of the nitrile and of the primary addition products and on the course of subsequent reactions is marked.

Like trifluoroacetonitrile, difluoronitroacetonitrile reacted readily with ammonia or primary or secondary alkylamines to form N-substituted difluoronitroacetamidines (I). However, satisfactory yields were obtained only when stoichiometric amounts of the amine were used,

$O_2NCF_2C(:NH)NRR'$

I

Ia. R = R' = H
Ib. R = CH_3, R' = H
Ic. R = R' = CH_3
Id. R = phenyl, R' = H
Ie. R = p-$CF_3C_6H_4$, R' = H

and low temperatures were required to avoid side reactions. Unlike trifluoroacetonitrile, difluoronitroacetonitrile also formed amidines from amines of low basicity such as aniline (Id) or even *p*-trifluoromethylaniline (Ie), but the reaction rates were lower. The physical properties of the amidines and their derivatives are listed in Table I. The amphoteric nature of difluoronitroacetamidine (Ia) was shown by its formation of both a silver salt and salts with acids such as trifluoroacetic or hydrobromic. The N-substituted amidines also showed evidence of formation of silver salts, but the salts were not obtained in a pure state. Trifluoroacetic acids salts of the substituted amidines were mostly low melting, but the hydrobromides were all crystalline. Two bands in the C═N region of the infrared spectrum of N-methyldifluoronitroacetamidine (Ib) indicate that this compound probably exists as an equilibrium mixture of the two possible tautomeric forms. Single bands in the C═N region of the spectra of the aromatically substituted derivatives (Id and Ie) indicate only one tautomer. Since both Id and Ie show doublets in the NH region, the double bond in these compounds is thought to be conjugated with the aromatic rings.

The amidines combined with a second equivalent of difluoronitroacetonitrile to produce (difluoronitroacetylimino)difluoronitroacetamidines (II) which could also be obtained directly from the nitrile by reaction with one-half equivalent of the amine.

$O_2NCF_2C(:NR)N{=}C(NR_2')CF_2NO_2$

IIa. R = R' = H
IIb. R = CH_3, R' = H
IIc. R = H, R' = CH_3
IId. R = phenyl, R' = H

N' - (Difluoronitroacetylimino)difluoronitroacetamidine (IIa) formed a water-insoluble copper chelate, but this ability was not shown by any of the substituted derivatives. None of the acetyliminoacetamidines formed silver salts.

Thermal decomposition of Ia gave difluoronitromethane as the only substantial volatile product. The remainder of the material appeared to be salts and/or polymers similar to those formed by the reaction of the amidine with excess ammonia. Difluoronitromethane, reported here for the first time, is a colorless liquid with a normal boiling point of 43.4° and a freezing point of approximately −120°. Its vapor pressure in the range from 300–800 mm. is given by the equation log $P_{\text{mm}} = 8.0187 - 1626.7/T_{°\text{K}}$. The heat of vaporization calculated[6] from this equation is 7188 cal./mole and the Trouton ratio is 22.7.

Compound IIa showed no tendency to react with a third equivalent of nitrile but decomposed, slowly at room temperature and more rapidly at higher temperatures, to difluoronitromethane and a sublimable, colorless solid melting at 76–77°. The latter was assigned the structure 3 - (difluoronitromethyl) - 1,2,4 - triazole (IIIa) on the basis of the following evidence. (1) Elementary analysis was consistent with the empirical formula $C_3H_2F_2N_4O_2$. (2) Infrared spectra showed bands corresponding to NH, CH, C═N, NO_2, and CF. (3) The F^{19} nuclear magnetic resonance spectrum in dimethyl sulfoxide solution showed only one unsplit

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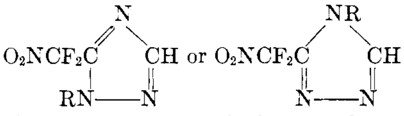
(5) W. L. Reilly and H. C. Brown, *J. Org. Chem.*, **22**, 698 (1957).

(6) G. W. Thomson, "Physical Methods of Organic Chemistry," Vol. I, Part 1, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p. 518.

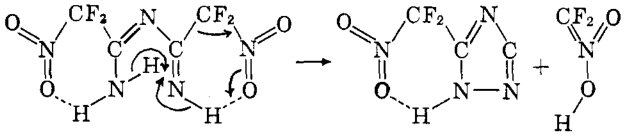
resonance. The proton spectrum showed two slightly broadened bands at −4.96 and −6.79 p.p.m. with respect to dimethyl sulfoxide. Neither was affected by dilution or by addition of water or pyridine. The higher field band was broadened essentially to the point of disappearance by acidification with dilute hydrochloric acid.[7] (4) The molecular weight as determined by the Rast method in *dl*-camphor was 169 (calcd. 164). (5) The ultraviolet absorption spectrum in aqueous solution showed a maximum at 206 mμ, $\epsilon_{\max}$ 6300. 1,2,4-Triazole is reported to absorb at 205 mμ, $\epsilon_{\max}$ 200.[8]



IIIa. R = H IIIb. R = CH_3

The N-monosubstituted-N-(difluoronitroacetylimino)difluoronitroacetamidines were decomposed to 2(or 4)-substituted-3-difluoronitromethyl-1,2,4-triazoles (IIIb), while the N,N-disubstituted derivative was thermally stable.

The increased reactivity of difluoronitroacetonitrile toward amines (as compared with the perfluornitriles) and the ease of cission of the C–C bond in the novel cyclization of the acyliminoamidines can reasonably be attributed to the higher electronegativity of the nitro compounds. In the ring closure reactions, the large steric requirements of the nitro group probably also play a part. In addition, internal hydrogen bonding between the amino and adjacent nitro groups and between the imino and its adjacent nitro group would be expected to have a pronounced effect on the spacial arrangement of the nitro containing acyliminoamidines and should strongly favor formation of a five-membered ring. A concerted reaction in which difluoronitromethane leaves as the *aci*-nitro acid is readily envisioned and requires migration of only a single proton. The failure of the N,N-disubstituted derivative to cyclize would be expected if such a mechanism were operative. This appears to be the first reported example of the closure of a 1,2,4-triazole ring by the formation of a N–N bond.



Experimental[9]

Difluoronitroacetamidine (Ia).—Difluoronitroacetonitrile[10] (0.02 mole) and ammonia (0.02 mole) were measured by standard vacuum techniques and were condensed by means of liquid nitrogen into an evacuated, 100-ml., Pyrex reaction bulb. The liquid nitrogen bath was then replaced by one of ethylene dichloride slush. After 1 hr. the reaction mixture was allowed to warm to room temperature, and volatile products and unchanged starting materials were pumped off into a liquid nitrogen-cooled trap on the vacuum manifold. The liquid remaining in the bulb was distilled at 80–90° and 5–10 μ to yield 1.79 g. (63%) of slightly yellow liquid. The major infrared absorption bands[11] were at 2.85 (m) (NH_2 asym. stretch), 2.92 (m) (NH_2 sym. stretch), 3.00 (m) (=NH stretch), 3.15 (m), 6.00 (s) (NC=N asym. stretch), 6.30 (s) (NO_2 asym. stretch), 6.90 (m), 7.40 (m) (NO_2 sym. stretch), 8.20 (s) (CF), 8.72 (m), 9.60 (m), 9.95 (m), 11.92 (m), and 12.30 (m).

With excess liquid ammonia under reflux at one atmosphere or with a one-to-one ratio at 0°, the yield was only 15–20%. The remainder of the reaction products were mainly nonvolatile, high melting (above 200°), water insoluble solids which are probably mixtures of salts and/or polymers arising from the reaction of the amidine with excess ammonia. Similar solids are formed during thermal decomposition of the amidine.

Silver Salt of Ia.—Silver oxide (0.30 g., 1.29 mmoles) suspended in 1 ml. of dry ether was treated with 0.36 g. (2.59 mmoles) of Ia. Heat was evolved and the brown oxide turned white. The mixture was stirred thoroughly by hand to break up lumps, and the precipitated silver salt was removed by centrifugation, washed twice with 1-ml. portions of ether and vacuum dried at room temperature and 2 μ for 18 hr. The nearly white salt does not melt below 200°, although there is some decomposition at lower temperatures, and darkening occurs gradually at room temperature on exposure to light.

Ia Trifluoroacetate.—The amidine (0.32 g., 2.31 mmoles) was treated for 1 hr. at room temperature with 0.79 g. (6.89 mmoles) of trifluoroacetic acid. Heat was evolved and a white precipitate formed almost immediately. The excess trifluoroacetic acid was removed at room temperature under reduced pressure, and the residue was washed twice with 3-ml. portions of ether and dried at room temperature and 1–2 μ for 20 hr.; m.p. 173–174° dec.

N-Methyl- and N,N-Dimethyldifluoronitroacetamidine(Ib and Ic).—The N-methyl and N,N-dimethyl derivatives were prepared as described. Major infrared absorption bands for Ib were at 2.97 (sh) (NHR stretch), 3.10 (m) (=NH stretch), 3.20 (m) (CH stretch), 6.00 (s) (NC=N asym. stretch), 6.10 (s) (NC=N asym. stretch), 6.33 (s) (NO_2 asym. stretch), 6.60 (sh), 6.90 (vw), 7.10 (w), 7.28 (m), 7.45 (m) (NO_2 sym. stretch), 8.35 (s) (CF), 9.80 (m), 10.40 (w) and 11.92 (m). For Ic they were at 3.05 (m) (=NH stretch), 3.45 (m) (CH stretch), 6.20 (s) (NC=N asym. stretch), 6.30 (s) (NO_2 asym. stretch), 7.10 (m), 7.40 (m) (NO_2 sym. stretch), 7.87 (w), 8.40 (s) (CF), 9.22 (m), 9.40 (sh), 9.80 (s), 11.40 (m), 12.20 (m), and 13.80 (m).

N-Phenyl- and N-(*p*-Trifluoromethylphenyl)difluoronitroacetamidine (Id and Ie).—The aromatic derivatives were prepared as described except that the amine was measured into the reactor and was frozen in liquid nitrogen prior to evacuation, the reaction temperature was 0°, and the reaction time was 18–24 hr. Major infrared absorption bands for Id were at 2.88 (m) (NH_2 asym. stretch), 2.98 (m) (NH_2 sym. stretch), 3.20 (w) (CH stretch), 5.95 (s) (NC=N asym. stretch), 6.30 (s) (NO_2 asym. stretch), 6.75 (m), 7.17 (m), 7.43 (m) (NO_2 sym. stretch), 8.05 (s), 8.50 (s) (CF), 9.35 (w), 9.80 (m), 10.05 (m), 11.00 (w), 11.89 (m), 12.05 (m), 12.80 (m), 13.65 (m), and 14.35. For Ie (KBr pellet) they were at 2.90 (m) (NH_2 asym. stretch), 3.10 (m) (NH_2 sym. stretch), 3.20 (m) (CH stretch), 6.00 (s) (NC=N asym. stretch), 6.30 (s) (NO_2 asym. stretch), 6.67 (w), 7.10 (w), 7.25 (w), 7.43 (s) (NO_2 sym. stretch), 8.00 (s), 8.40 (m) (CF), 8.63 (m), 9.00 (s), 9.37 (s), 9.85 (m), 10.10 (m), 11.46 (m), 11.90 (m), 12.02 (m), 12.80 (m), 13.38 (w), and 13.80 (w).

Hydrobromides.—Hydrobromides were prepared by saturating ether solutions of the amidines with hydrogen bromide gas, centrifuging, washing with ether, and drying at room temperature and 5–10 μ for 8–18 hr. The hydrobromides were somewhat hydroscopic and were readily hydrolized in hydroxylic solvents.

N′-(Difluoronitroacetylimino)difluoronitroacetamidine (IIa).

A. From Difluoronitroacetamidine.—Difluoronitroacetamidine (1.19 g., 8.56 mmoles) was treated with 8.83 mmoles of difluoronitroacetonitrile at 0° for 18 hr. Removal of unreacted nitrile and distillation at 100–110° and 5–10 μ yielded 1.25 g. (56%) of slightly yellow liquid. Major infrared absorption bands were located at 2.95 (s) (NH stretch), 3.06 (m) (=NH stretch), 3.2 (sh), 3.48 (w), 3.8 (w), 6.09 (s) (NC=N asym. stretch, 6.30 (s) (NO_2 asym. stretch), 6.59 (s), 7.3 (sh), 7.46 (s) (NO_2 sym.

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[7] The proton n.m.r. spectrum of 3-amino-1,2,4-triazole in dimethyl sulfoxide showed two bands at −3.25 and −4.87 p.p.m. with respect to dimethyl sulfoxide. The higher field band was broadened essentially to the point of disappearance by acidification.

[8] H. A. Staab, *Chem. Ber.*, **89**, 1927 (1956).

[9] Melting points are corrected; boiling points except for that of difluoronitromethane are not corrected.

[10] I. L. Knunyants and A. V. Fokin, *Dokl. Akad. Nauk, SSSR*, **112**, 67 (1957).

[11] Infrared spectra were taken on a Perkin-Elmer Infracord Model 137 spectrophotometer as liquids unless otherwise noted. The units are microns.

stretch), 8.2 (s) (CF), 8.75 (w), 9.62 (s), 10.03 (m), 11.59 (m), 11.91 (m), 12.30 (s), 12.78 (m), 13.7 (w), and 14.1 (w).

B. **From Difluoronitroacetonitrile.**—Difluoronitroacetonitrile (0.02 mole) and ammonia (0.01 mole) were condensed into an evacuated 150-ml. Pyrex bulb. The bulb then was placed in an ice bath for 18–24 hr. Volatiles were removed on the vacuum manifold, and the liquid product was distilled as before to yield 2.34 g. (86%) of IIa. Its infrared spectrum was identical with that of material prepared from the amidine. If ratios of nitrile to ammonia of greater than two to one were employed, only two equivalents of nitrile were consumed; the remainder could be recovered quantitatively.

Copper Chelate of IIa.—IIa (0.20 g., 1.25 mmole) dissolved in 0.5 ml. of 1,2-dimethoxyethane was shaken with a solution of 0.15 g. (0.66 mmole) of cupric nitrate trihydrate in 1.0 ml. of water. The precipitated, rust-colored solid was removed by centrifugation, washed twice with 0.5-ml. portions of water, and dried at room temperature and 5 μ for 5 hr.; weight 0.17 g. (48%). After one recrystallization from benzene containing a few drops of 95% ethanol, it melted above 200°. It was very soluble in 95% ethanol, forming dark maroon solutions.

N-Methyl- and N,N-Dimethyl-N′-(difluoronitroacetylimino)-difluoronitroacetamidine (IIb and IIc).—IIb and IIc were prepared by method B. Major infrared absorption bands for IIb were at 2.97 (m) (NH stretch), 3.20 (w), 3.45 (w) (CH stretch), 5.93 (s) (NC═N asym. stretch), 6.03 (s) (NC═N asym. stretch), 6.30 (s) (NO_2 asym. stretch), 6.55 (m), 6.90 (w), 7.09 (w), 7.40 (m) (NO_2 sym. stretch), 7.65 (w), 8.25 (s) (CF), 8.83 (w), 9.38 (m), 9.80 (m), 10.20 (m), 11.60 (w), 11.90 (m), 12.00 (w), 12.20 (m), 12.35 (m), 12.80 (m), 13.1 (w), and 13.8 (w). For IIc they were at 3.00 (w) (═NH stretch), 3.47 (m) (CH stretch), 6.20 (s) (NC═N asym. stretch), 6.30 (s) (NO_2 asym. stretch), 6.70 (m), 7.08 (m), 7.48 (m) (NO_2 sym. stretch), 8.00 (s), 8.20 (s) (CF), 8.45 (w), 8.65 (m), 9.70 (m), 10.20 (m), 11.63 (m), 11.83 (m), 12.03 (w), 12.17 (m), 12.40 (m), and 12.80 (m).

N-Phenyl-N′-(difluoronitroacetylimino)difluoronitroacetamidine (IId).—The phenyl compound was prepared by method B except that the amine was measured into the reactor and was frozen in liquid nitrogen prior to evacuation, and the 0° reaction period was followed by an additional 24 hr. at room temperature. Major infrared absorption bands were at 3.00 (w) (═NH stretch), 6.00 (s) (NC═N asym. stretch), 6.30 (s) (NO_2 asym. stretch), 6.80 (m), 7.20 (w), 7.45 (m) (NO_2 sym. stretch), 8.15 (s) (CF), 8.40 (m), 9.40 (w), 9.78 (w), 11.00 (w), 11.90 (m), 12.10 (m), 12.85 (w), 13.2 (w), 13.7 (w), and 14.4 (m).

Difluoronitromethane.—Difluoronitroacetamidine (0.40 g., 2.91 mmoles) was heated for 3 hr. at 95–105° under 400 mm. of helium. Difluoronitromethane (1.77 mmoles, 61%) was collected in a liquid nitrogen-cooled trap atop a short air condenser. Major infrared absorption bands for the vapor were at 3.30 (w), 3.40 (w) (CH stretch), 3.70 (vw), 4.36 (vw), 6.22 (s) (NO_2 asym. stretch), 7.38 (m) (NO_2 sym. stretch), 7.60 (m), 8.55 (s), 10.70 (m), and 12.5 (m). Approximately 50% yields could be obtained by similar thermal decomposition of IIa or IIb. The molecular weight as determined by PVT measurements was 96.4 (calcd. 97.0).

3-Difluoronitromethyl-1,2,4-triazole (IIIa).—IIa (1.68 g., 6.44 mmoles) was heated at 120° for 3 hr. under 400 mm. of helium. The difluoronitromethane which was evolved was collected in a liquid nitrogen-cooled trap atop a short air condenser and amounted to 5.24 mmoles. Heating for an additional 24 hr. at 100–110° under 400 mm. of helium resulted in evolution of an additional 0.21 mmole of difluoronitromethane. Heating the residue at 100–110° at 1 μ caused sublimation of 0.53 g. (50%) of crystalline triazole melting at 73.5–76°. After two recrystallizations from benzene–petroleum ether, it melted at 76–77° (unchanged by sublimation at 100° and 1 μ). The yield was essentially the same if the triazole was prepared directly from difluoronitroacetonitrile without isolation of the intermediate IIa. Major infrared absorption bands (KBr pellet) were at 2.90 (s) (NH stretch), 2.95 (s) (NH stretch), 3.08 (s) (NH stretch), 3.10 (sh), 3.40 (vw) (CH stretch), 3.70 (vw) (NH ammonium type band), 4.10 (vw), 6.03 (s) (NC═N asym. stretch), 6.30 (s) (NO_2 asym. stretch), 6.55 (s), 7.00 (w), 7.14 (w), 7.37 (m) (NO_2 sym. stretch), 8.20 (vs) (CF), 9.33 (m), 9.52 (m), 9.70 (m), 10.18 (s), 10.62 (m), 11.59 (m), 11.99 (m), 12.13 (s), 12.78 (s), 13.22 (w), 13.80 (w), and 14.7 (w).

3-Difluoronitromethyl-2(or 4)-methyl-1,2,4-triazole(IIIb).—Difluoronitroacetonitrile (0.02 mole) and methylamine (0.01 mole) were condensed into a 60-ml. evacuated Pyrex bulb. After 20 hr. at 0° the bulb was filled to a pressure of 400 mm. with helium and heated at 100–110° for 7 hr. Difluoronitromethane (5 mmoles, 25% based on nitrile) evolved during the heating was collected in a liquid nitrogen-cooled trap. The liquid remaining in the reaction bulb was distilled at 130–140° and 2–5 μ to yield 1.20 g. (33%) of light yellow liquid. Major infrared absorption bands were at 2.90 (m) (NH stretch), 3.40 (CH stretch), 5.95 (sh) (NC═N asym. stretch), 6.15 (s) (NC═N asym. stretch), 6.30 (s) (NO_2 asym. stretch), 6.55 (m), 6.90 (w), 7.09 (m), 7.41 (m) (NO_2 sym. stretch), 8.10 (s) (CF), 8.85 (w), 9.70 (w), 10.20 (m), 11.60 (w), 12.00 (w), 12.20 (m), and 12.80 (m).

Acknowledgment.—The author is indebted to Robert Lim and Elinor R. Smathers for the microchemical analyses and to Douglas B. Fields for preparation of part of the difluoronitroacetonitrile and for obtaining some of the infrared spectra. James A. Happe provided the nuclear magnetic resonance data.

Addition Compounds of Thiols and 1-Substituted Nicotinamides[1,2]

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Received December 10, 1962

van Eys and Kaplan have observed that "the ubiquitous nature of sulfhydryl compounds in biological systems" makes the addition reactions of thiols and diphosphopyridinenucleotide[5] (DPN) and its analogs of "particular interest."[6] The addition of a sulfhydryl enzyme to the 4-position of DPN has been suggested as an intermediate in the oxidation of aldehydes catalyzed by glyceraldehyde-3-phosphate dehydrogenase.[7]

Evidence for the addition of sulfide ion and of thiols to DPN has been adduced from changes in ultraviolet spectra.[6,8]

Wallenfels and Schüly have reported the synthesis of addition compounds of nicotinamide-1-(2,6-dichlorobenzylo) bromide and sulfide ion, benzyl mercaptan, 2-mercaptothiazole, β-phenylethyl mercaptan, ethyl mercaptan, thiocyanate ion, and thiophenol.[9]

In connection with investigations of some model systems for enzymic oxidation and reductions, new adducts of L-cysteine ethyl ester, ethyl thioglycolate, and *n*-propyl mercaptan with nicotinamide-1-(2,6-dichlorobenzylo) bromide have been prepared by addition of the mercaptan in aqueous sodium hydroxide to an aqueous solution of the quaternary bromide. These addition compounds were isolated as crystalline solids and their infrared and ultraviolet spectra were similar to each other.

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(1) This research was supported in part by the National Science Foundation, grant 7582.

(2) Taken from J. M. Kolyer, Ph.D. thesis, University of Pennsylvania, 1960.

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(4) Walter T. Taggart Memorial Fellow, 1959–1960.

(5) Nicotinamide–adenine-dinucleotide.

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