Oxadiazines and Dioxazines from Perhaloacetones and Cyanamides

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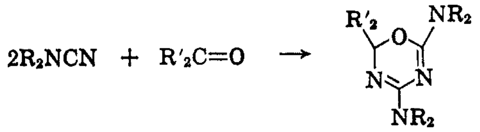
The reactions of hexafluoroacetone and dichlorotetrafluoroacetone with cyanamide, dimethylcyanamide, and diallylcyanamide give new 1,3,5-oxadiazines, 1,3,5-dioxazines, and ureas, depending on the mole ratios and reaction conditions. The dioxazines decompose with loss of ketone to perhaloalkylideneureas. In addition the oxadiazines and dioxazines from cyanamide undergo thermal rearrangement to dihydrotriazine and dihydrooxadiazine derivatives, respectively.

Russian workers have reported that aliphatic ketones and cyanamide react to give alkylidenecyanamides ($R_2C{=}NCN$).[1]

Newallis and Rumanowski have prepared a series of 1:1 adducts from urea and other primary amides with fluoro ketones.[3]

We have found that hexafluoroacetone and dichlorotetrafluoroacetone react with cyanamides to give several different products depending upon the reaction conditions and mole ratio of reactants.

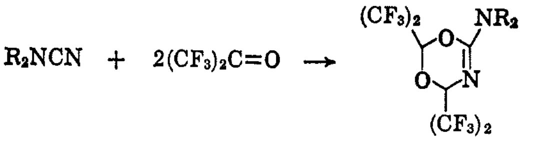
The reactions of dialkylcyanamides with perhaloacetones are less complex and will be considered first. Hexafluoroacetone reacts with excess dimethylcyanamide at 175° to give 91% of crystalline 2,4-bis(dimethylamino)-6,6-bis(trifluoromethyl)-2H-1,3,5-oxadiazine (Ic). The new oxadiazine is stable in air at its boiling point (250°) and in boiling aniline. Analogous oxadiazines have been obtained from diallylcyanamide and hexafluoroacetone as well as from dimethylcyanamide and 1,3-dichlorotetrafluoroacetone (Ie and Id, respectively).



Ia, R = H^-; R′ = CF_3^-
b, R = H^-; R′ = CF_2Cl^-
c, R = CH_3^-; R′ = CF_3^-
d, R = CH_3^-; R′ = CF_2Cl^-
e, R = $CH_2{=}CHCH_2^-$; CF_3^-

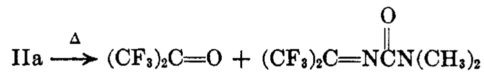
The structure assignment of the oxadiazine (Ic) is substantiated by elemental analysis, molecular weight, infrared (no OH or NH stretching; two C=N bands at 5.65 and 5.90 μ), and nmr [single $N(CH_3)_2$ at τ 7.0].

The reaction of excess hexafluoroacetone with dimethylcyanamide at 150° gives a 96% yield of an unstable liquid, 6-dimethylamino-2,2,4,4-tetrakis(trifluoromethyl)-4H-1,3,5-dioxazine (IIa). While the analytical data are not completely satisfactory, the infrared absorption at 5.90 μ with no OH or NH and the nmr spectrum indicate the crude product is mainly IIa.



IIa, R = CH_3
b, R = H

Upon vacuum distillation or prolonged storage, IIa loses 1 mole of hexafluoroacetone and 1,1-dimethyl-3-hexafluoroisopropylideneurea (III) is formed. Structure III is confirmed by elemental analysis, molecular



$$\text{IIa} \xrightarrow{\Delta} (CF_3)_2C{=}O + (CF_3)_2C{=}N\overset{O}{\overset{\|}{C}}N(CH_3)_2$$

III

weight, proton nmr spectrum, and infrared spectrum (C=N and C=O absorption at 5.82 and 5.94 μ). Reaction of III with aqueous base is vigorous and gives dimethylamine. (Tetramethylurea undergoes a similar reaction.)

Reaction of approximately equimolar amounts of cyanamide with hexafluoroacetone or 1,3-dichlorotetrafluoroacetone at less than 25° followed by heating at 50–55° produces 4,6-diamino-2,2-bis(perhalomethyl)-2H-1,3,5-oxadiazines (Ia and b). These products are analogous to Ic and d; however, their formation at low temperature and the isolation of an unstable 1:1 intermediate suggest that the reaction involves addition of cyanamide to the fluoro ketone to produce the hydroxyalkylcyanamides IV.

$$R_2C{=}O + NH_2CN \longrightarrow R_2\overset{OH}{\overset{|}{C}}NHCN$$

IVa, R = CF_3
b, R = CF_2Cl

The oil IVb prepared from cyanamide and dichlorotetrafluoroacetone may be pumped free from fluoro ketone and shows OH and/or NH and C≡N absorption in the infrared. This oil, when heated for a few minutes at 100°, forms 52% of dichlorotetrafluoroacetone and 54% of Ib. Both Ia and b can be prepared in high yield by heating IV in toluene at 50–55° for 20–24 hr.

The structures of Ia and b were deduced by elemental analysis and similarity of the infrared spectra to those of Ic and d. The C=N stretching vibrations of Ia and b are at 5.70 and 5.95 μ, almost identical with those of the bisdimethylaminooxadiazine Ic. This indicates that Ia and b exist in the amino tautomeric form. The 3-μ infrared region shows a complex band pattern, an outstanding feature of which is the nonbonded NH_2 at 2.85 μ. This sharp peak is present in all com-

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[1] (a) B. J. Sukhorukov, *Opt. i Spectroskopiya*, **9**, 46 (1960); *Chem. Abstr.*, **54**, 2386*i* (1960); (b) N. A. Goldberg and V. G. Golov, *Khim. Nauka i Promy*, **4**, 138 (1959); *Chem. Abstr.*, **54**, 10507*e* (1960). These authors have undoubtedly misidentified their high-melting, rather intractable, solid, ketone–cyanamide reaction products as monomeric alkylidenecyanamides.[2]

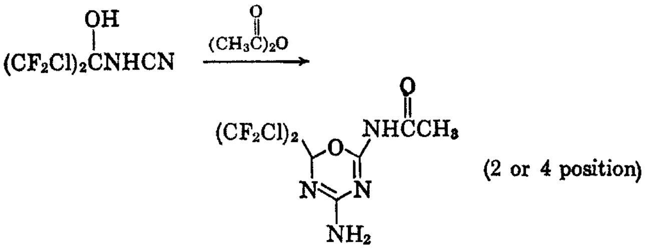
[2] F. D. Marsh and M. E. Herme [*J. Am. Chem. Soc.*, **86**, 4506 (1964) have prepared monomeric alkylidenecyanamides from olefins and cyanogen azide and have found them to be mobile oils, easily hydrolyzed to cyanamide and the corresponding ketone.

[3] P. E. Newallis and E. J. Rumanowski, *J. Org. Chem.*, **29**, 3114 (1964).

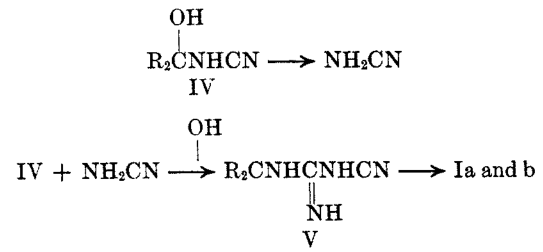
pounds in this series in which an NH_2 group is believed to be present.

The oxadiazines Ia and b show a single proton magnetic resonance line at τ 3.1 in dimethyl sulfoxide.[4] There is no particular broadening of this resonance on cooling so that it is believed that the single line represents coincidental chemical shifts of the two amino groups and not time averaging of the various tautomeric forms.

Attempted acetylation of IVb at 50° using acetic anhydride gave a small amount of monoacetyl Ib in which the location of the acetyl group has not been determined. The infrared spectrum of this compound shows the two C=N stretching frequencies, a C=O at 6.04 μ and slightly modified NH_2 and NH in the 3-μ region. However, a sharp nonbonded NH_2 absorption is present at 2.95 μ. The proton resonance shows the NH_2 at τ 2.8 and the more acidic NH shifted to τ −0.7. Attempts to prepare this compound by acetylation of Ib at 140° led to a new, isomeric acetyl derivative arising from ring rearrangement (to be discussed in a following section).



Formation of Ia and b may involve reaction of cyanamide generated by pyrolysis of IV with unchanged IV to give V. To test this hypothesis, 1,3-dichlorotetrafluoroacetone was added to dicyandiamide which was expected to produce V directly or its cyclic isomer Ib. This result was not achieved since the product, formed in 78% yield, was composed of ketone–dicyandiamide (1:2). The structure of this compound has eluded us, but will be discussed later.

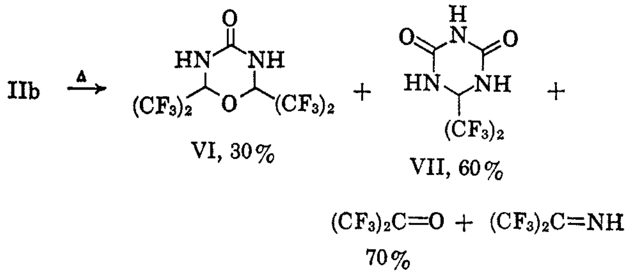


$$\underset{\mathrm{IV}}{\mathrm{R_2\overset{OH}{C}NHCN}} \longrightarrow \mathrm{NH_2CN}$$

$$\mathrm{IV + NH_2CN} \longrightarrow \underset{\mathrm{V}}{\mathrm{R_2\overset{OH}{C}NH\underset{NH}{\underset{\|}{C}}NHCN}} \longrightarrow \mathrm{Ia\ and\ b}$$

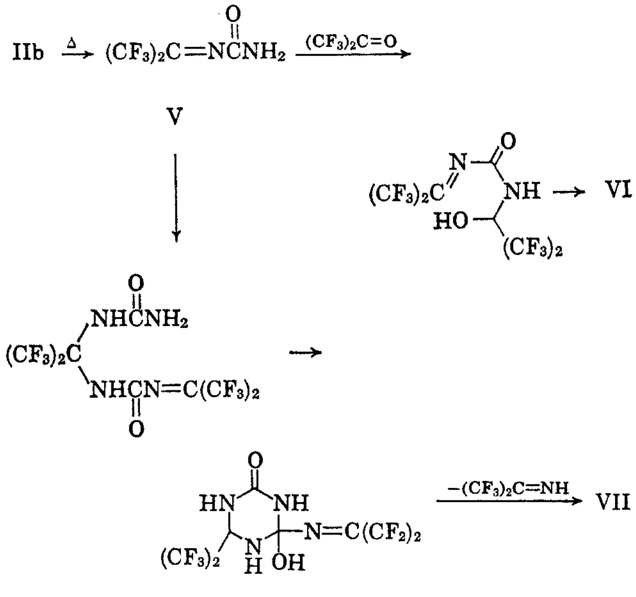
Addition of cyanamide to a fourfold excess of hexafluoroacetone at −15 to 0° results in a 72% yield of 2,2,4,4-tetrakis(trifluoromethyl)-6-amino-4-H-1,3,5-dioxazine (IIb) which is stable to storage at room temperature. The C=N stretching band of IIb is at 5.80 μ, and the general appearance of the spectrum indicates its similarity to IIa. The 3-μ region in the infrared is quite similar to Ia and b and shows nonbonded NH_2. Proton resonance in dimethyl sulfoxide gives a single resonance line at τ 1.8. We feel that the amino tautomer again predominates because of the single pmr line, the NH_2 in the infrared, and similarity of the C=N region with that of IIa in which the dimethylamino structure is, of necessity, present. On heating for a few minutes at 110–130° in xylene, IIb is converted to several products. A 31% yield of isomeric tetrahydro-2,2,6,6-tetrakis(trifluoromethyl)-4H-1,3,5-oxadiazine-4-one (VI) is obtained. Essentially 100% of 1 mole of hexafluoroacetone based on the unisomerized portion of IIb is obtained along with 4,4-bis(trifluoromethyl)-hexahydro-2,6-dioxo-1,3,5-triazine (VII)[5] (59% based on 0.5 mole/mole of unisomerized IIb, Scheme I) and 30% of hexafluoroacetone imine (calculated similarly). The structure of VI was deduced from analysis, and single NH absorption at τ −0.3 in dimethyl sulfoxide (DMSO), infrared absorption at 5.90 μ, and lack of sharp, nonbonded NH_2 stretching present in Ia, b, IIb, and acetyl Ib.

Scheme I



Loss of hexafluoroacetone from IIb may give hexafluoroisopropylideneurea (as IIa → III) and the products may arise from the urea by (a) addition of hexafluoroacetone to the NH_2 and cyclization to give VI (Scheme II), and (b) dimerization of the urea by addition of NH_2 across the C=N, cyclization, and loss of hexafluoroacetoneimine.

Scheme II



It has also been found that Ib rearranges on pyrolysis. On heating IVb for 2 hr at 95° in toluene 41% of Ib is obtained; however, continued heating for 20 hr gives 26% of an isomeric material. The most likely mechanism for isomeric action involves ring opening and subsequent cyclization to 4-amino-6,6-bis(chlo-

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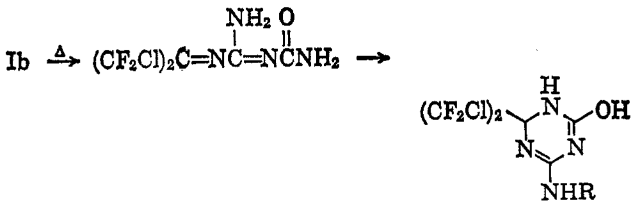
[4] S. Gronowitz and R. A. Hoffman, [*Arkiv Kemi*, **16**, (39) 459 (1960)] reported absorption for 2-aminopyrimidine at τ 3.4 in this same solvent.

[5] Identical with that prepared by W. J. Middleton and C. G. Krespan *J. Org. Chem.*, **30**, 1398 (1965).



VIII, R = H
IX, R = Ac

rodifluoromethyl)-1,6-dihydro-5-triazin-2-ol (VIII). Heating of Ib for 15 min at 215° in 1,2,4-trichlorobenzene solution gives VIII in 70% yield.

The tautomeric structure VIII is tentatively assigned on the basis of spectral data. The nmr spectrum in DMSO at 20° shows three sharp absorbances in a ratio of 2:1:1. The high-field resonance at τ 3.9 is in a reasonable position for NH_2 while two single absorptions are present at τ 1.1 and 0.6. As the temperature is increased to 70° the NH_2 broadens slightly while the two single absorbances broaden considerably. At 120°, the low-field lines have coalesced to a broad peak while the NH_2 broadens but remains separate. At 170° one broad absorbance is observed. On cooling below room temperature, all three peaks sharpen. These data suggest the presence of an NH_2 group and two separate protons which equilibrate much more rapidly with each other than with the NH_2 protons. The infrared shows a band for NH_2 at 2.83 μ and one at 3.40 μ which can be attributed to bonded OH, as well as bands at 5.80 and 5.95 μ which are assigned to C=N stretching. The band shapes are similar to those in the spectrum of Ia and b except that the more intense band is at longer wavelength (5.80 *vs.* 5.70 μ in Ia and b).

Treatment of Ib with acetic anhydride at 140° gives the acetyl derivative IX. The infrared spectrum shows no free NH_2 group; nmr signals occur in a 1:1:1 ratio at τ −0.4, 0.4, and 1.4. This derivative can be prepared directly from VIII under the same conditions.

The unknown adduct obtained from dichlorotetrafluoroacetone and dicyandiamide has pmr absorption in dimethyl sulfoxide at τ 3.2 (2 H), −0.3 (1 H), and −0.8 (1 H). On cooling, the high-field peak clearly separates into two single peaks of equal intensity indicating rapid equilibrium between forms in solution. The infrared spectrum indicates presence of an NH_2 but the general appearance of the spectrum indicates that the compound may have a linear rather than cyclic structure.

Experimental Section

Materials.—Dichlorotetrafluoroacetone was obtained from the General Chemical Division of Allied Chemical Corp. Cyanamide was obtained as a 20% ether solution from Eastman Organic Chemicals.

2,4-Diamino-6,6-bis(trifluoromethyl)-2H-1,3,5-oxadiazine (Ia).—An ether solution (22 ml) containing 4.2 g (0.10 mole) of cyanamide was added to 16.6 g (0.10 mole) of hexafluoroacetone while the temperature was held below 15°. The solvents were evaporated at 15 mm after allowing the solution to stand for 2 hr at 0°. The residual oil was dissolved in 100 ml of toluene and heated at 50° for 20 hr. Filtration gave 7.25 g (58%) of Ia: mp 176–176.5° after recrystallization from acetone–acetonitrile; $\lambda_{\max}^{\text{KBr}}$ 2.88, 3.06, 3.12, 3.20 (NH), 5.70, and 5.97 μ (C=N).

Anal. Calcd for $C_5H_4F_6N_4O$: C, 24.0; H, 1.6; F, 45.7; N, 22.4. Found: C, 24.2; H, 2.0; F, 44.0; N, 22.1.

2,4-Diamino-6,6-bis(chlorodifluoromethyl)-2H-1,3,5-oxadiazine (Ib).—A solution of 42.0 g (1.0 mole) of cyanamide in 200 ml of anhydrous diethyl ether was added to 1,3-dichlorotetrafluoroacetone (300.0 g, 1.5 moles) in 200 ml of ether at 25° using ice-bath cooling. An hour after mixing, the excess ketone and solvent were removed by evaporation. The residual oil was heated with 400 ml of benzene at 51–52° for 64 hr. Filtration gave white needles: mp 214.5°; $\lambda_{\max}^{\text{KBr}}$ 2.85, 3.05, 3.10, 3.18 (NH), 5.70, and 5.95 μ (C=N). Ib showed end absorption only in the ultraviolet.

Anal. Calcd for $C_5H_4Cl_2F_4N_4O$: C, 21.2; H, 1.4; F, 26.8. Found: C, 21.4; H, 1.5; F, 26.4.

Recrystallization from acetone gave crystals containing 0.5 mole of acetone of crystallization: mp 188°.

Anal. Calcd for $C_5H_4Cl_2F_4N_4O \cdot 0.5C_3H_6O$: C, 25.0; H, 2.3; Cl, 22.7; F, 24.3; N, 17.9. Found: C, 25.2; H, 2.7; Cl, 22.7; F, 24.3; N, 18.0.

Heating this material at 70° for 16 hr gives pure Ia.

2,4-Bis(dimethylamino)-6,6-bis(trifluoromethyl)-2H-1,3,5-oxadiazine (Ic).—A mixture of 34.0 g (0.485 mole) of dimethylcyanamide and 39.8 g (0.24 mole) of hexafluoroacetone was heated for 6 hr at 175° in a stainless steel bomb at autogenous pressure. The solid product was recrystallized from ethyl acetate to give 67.0 g (91.2%) of 2,4-bis(dimethylamino)-6,6-bis(trifluoromethyl)-2H-1,3,5-oxadiazine as colorless needles, mp 136°. The proton nmr showed a singlet at τ 7.0 [$N(CH_3)_2$ protons]. The infrared spectrum contained no bands in the OH and NH regions, $\lambda_{\max}^{\text{KBr}}$ 5.65 and 5.90 μ (>C=N).

Anal. Calcd for $C_9H_{12}F_6N_4O$: C, 35.3; H, 4.0; F, 37.2; N, 18.3; mol wt, 306. Found: C, 35.4; H, 4.2; F, 37.0; N, 18.5; mol wt (ebullioscopic method in ethylene chloride), 307.

The product is stable at its boiling point (250°) in air and was quantitatively recovered after heating at 180° for 2 hr.

2,4-Bis(dimethylamino)-6,6-bis(chlorodifluoromethyl)-2H-1,3,5-oxadiazine (Id).—There resulted a 3° exotherm upon mixing dimethylcyanamide (70.0 g, 1.0 mole) with dichlorotetrafluoroacetone (199.0 g, 1.0 mole). The solution was heated for 4 hr at 45° and left at room temperature for 1 week. Pure crystals of Id separated, 55.0 g (32.5%), mp 160°.

Anal. Calcd for $C_9H_{12}Cl_2F_4N_4O$: C, 31.8; H, 3.6; Cl, 20.9; N, 16.5. Found: C, 31.5; H, 3.7; Cl, 20.9; N, 16.4.

2,4-Bis(diallylamino)-6,6-bis(trifluoromethyl)-2H-1,3,5-oxadiazine (Ie).—A mixture of 41.0 g (0.366 mole) of diallylcyanamide and 28.2 g (0.17 mole) of hexafluoroacetone was heated for 4 hr at 150° in a stainless steel bomb. The product was stripped at 25° (0.1 mm) to give a colorless oil.

Anal. Calcd for $C_{17}H_{20}F_6N_4$: N, 13.6. Found: N, 13.4.

6-Dimethylamino-2,2,4,4-tetrakis(trifluoromethyl)-4H-1,3,5-dioxadine (IIa) and 1,1-Dimethyl-3-hexafluoroisopropylidenylurea (III).—Dimethylcyanamide (14.0 g, 0.2 mole) and 75.0 g (0.45 mole) of hexafluoroacetone were heated at 150° for 8 hr in a stainless steel bomb. The bomb was cooled to 0°, and excess ketone was vented. The infrared spectrum of the crude product, 80.0 g (99.5%), indicated that it was essentially pure IIa. The analysis of IIa is not as exact as desired because of its instability, but the infrared spectrum (no OH, NH, or C=N absorption and a single C=N band at 5.90 μ) and proton nmr spectrum (single peak at τ 8.0 [$N(CH_3)_2$ protons] indicate that the proposed structure is correct.

Anal. Calcd for $C_9H_6F_{12}N_2O_2$: C, 26.8; H, 1.5; F, 56.7. Found: C, 27.5; H, 1.8; F, 55.5.

Fractionation of IIa on a spinning-band column resulted in the elimination of 1 mole of hexafluoroacetone (recovered from Dry Ice trap) and formation of 29.2 g (62.0% based on dimethylcyanamide) of 1,1-dimethyl-2-hexafluoroisopropylideneurea, bp 65° (22 mm), $n^{25}D$ 1.3556. The infrared spectrum contained no OH, NH, or C≡N bands. In the proton nmr the dimethylamino protons appear as two equal peaks, $\lambda_{\max}^{\text{KBr}}$ 5.82 (C=N) and 5.94 μ (C=O).

Anal. Calcd for $C_6H_6F_6N_2O$: C, 30.5; H, 2.6; F, 48.3; N, 11.9; mol wt, 236. Found: C, 30.7; H, 2.5; F, 48.3; N, 12.1; mol wt (cryoscopic method in benzene), 240.

4-Amino-6,6-bis(chlorodifluoromethyl)-1,6-dihydro-*s*-triazin-2-ol (VIII).—Cyanamide (12.3 g, 0.30 mole) in ether was added to dichlorotetrafluoroacetone (90 g, 0.45 mole), and the solution was allowed to warm spontaneously. The solution was heated further, and ether and ketone were distilled off until the temperature reached 95°. After heating at this temperature for 2 hr, filtration afforded 17.3 g (41%) of Ib contaminated with a small amount of IVb. Further heating of the solution for 20 hr gave 11 g (26%) of impure VIII. Three recrystallizations from ethyl acetate gave pure VIII: mp 298–299°; λ_{max}^{KBr} 2.83, 3.05, 3.10, 3.19 (NH), 5.80, 5.95 (C=N), 6.14, and 6.51 μ (NH bending); λ_{max}^{EtOH} 212 mμ (ε 2820).

Anal. Calcd for $C_5H_4Cl_4F_8N_4O$: C, 21.2; H, 1.4; Cl, 25.1; F, 26.8; mol wt, 283. Found: C, 21.6; H, 1.7; Cl, 25.0; F, 26.3; mol wt (cryoscopic in dimethyl sulfoxide), 267.

2,2,4,4-Tetrakis(trifluoromethyl)-6-amino-4H-1,3,5-dioxazine (IIb).—A solution of 4.95 g (0.12 mole) of cyanamide in 30 ml of ether was added to 80 g (0.48 mole) of hexafluoroacetone in 125 ml of ether over a 10-min period. The temperature rose from −15 to −2° and was held at −2° for 1.5 hr. The volatile solvent and excess hexafluoroacetone were then removed under vacuum at room temperature and an oil resulted. The oil was taken up in methylene chloride and extracted with water and the organic solution was dried and evaporated to give 32.3 g (72%) of crude IIb. The product was crystallized from pentane to give pure IIb: mp 67–69°; λ_{max}^{KBr} 2.87, 3.05, 3.10, 3.16 (NH), and 5.80 μ (C=N).

Anal. Calcd for $C_7H_2F_{12}N_2O_2$: C, 22.4; H, 0.5; F, 60.4; N, 7.5. Found: C, 22.8, 22.7; H, 0.9, 0.7; F, 60.7, 60.8; N, 7.9, 8.0.

Decomposition of IIb.—A solution of 6.65 g (0.0178 mole) of IIb in 50 ml of xylene was heated for 1 hr at 110–130°. A total of 2.0 g of hexafluoroacetone was collected in a cold trap after passing through a 0° condenser. On cooling, 3.0 g of crystalline material separated and was collected, which on the basis of proton nmr was shown to consist of 2.08 g of VI and 0.92 g of VII.

Sublimation of the mixture (1.0 g) at 90° (1 mm) gave 0.60 g of pure tetrahydro-2,2,6,6 tetrakis(trifluoromethyl)-4H-1,3,5-oxadiazin-4-one (VI), mp 175–177°, isomeric with IIb; λ_{max}^{Nujol} 3.1, 3.22 (NH), 5.84 (C=O), and 6.70 μ (NH bend).

Anal. Found: C, 21.6, 21.6; H, 0.6, 0.7; F, 59.5; N, 7.6, 7.7.

Continued sublimation at 90–130° causes some VII to sublime, however, it deposits in a second layer closer to the heat source. Sublimation was continued at 130° until no further VI was observed and the temperature was raised to 170° whereupon the bulk of VII sublimed and was collected (0.20 g): mp 222–226°; λ_{max}^{Nujol} 3.1, 3.25 (NH), 5.78, 5.90 (C=O), and 6.60 μ (NH bend).

Anal. Calcd for $C_5H_3F_6N_3O_2$: C, 23.9; H, 1.6; F, 45.4; N, 16.7. Found: C, 23.7; H, 1.2; F, 45.7; N, 16.7.

In a second experiment the volatiles collected after decomposition under vacuum were shown by mass spectrometry to be ~85% hexafluoroacetone and ~15% hexafluoroacetone imine.

Preparation of VIII from Ib.—A solution of 10 g of Ib in 500 ml of 1,2,4-trichlorobenzene was heated for 15 min at 215°. The solution was quickly filtered and after cooling 7.0 g of VIII (70%) was isolated by filtration.

Pyrolysis of (1:1) Ketone-Cyanamide Adduct.—The oil IVb (14g) formed by contacting cyanamide and dichlorotetrafluoroacetone at 0–10°, followed by evaporation of the solvents, was heated at 100° for a few minutes. Dichlorotetrafluoroacetone (3g, 52%) was recovered along with 4.4 g (54%) of Ib.

Preparation of Acetyl Ib.—Approximately 24 g (0.1 mole) of the above oil IVb was heated at 52° for 16 hr with 10.2 g (0.10 mole) of acetic anhydride. Filtration gave 2.2 g (7%) of acetyl compound which melted at 222–222.5° after recrystallization from acetone–ether: λ_{max}^{KBr} 2.95, 3.04, 3.09, 3.14 (NH), 5.64, 5.88 (C=N), 6.04 (C=O), and 6.53 μ (–NH bend).

Anal. Calcd for $C_7H_6Cl_2F_4N_4O_2$: C, 25.9; H, 1.9; Cl, 21.9; F, 23.4; N, 17.2. Found: C, 26.0; H, 2.0; Cl, 21.5; F, 23.1; N, 17.0.

Attempted Preparation of Acetyl Derivative from Ib. Formation of IX.—A solution of 6 g (0.021 mole) of Ib was refluxed for 2 hr in 100 ml of acetic anhydride. The solution was evaporated to 20 ml, and ether was added along with decoloring charcoal. After allowing this mixture to stand for 1 hr, the ether was evaporated, methanol was added, and the whole solution was filtered into water to give 3.3 g (45%) of IX. After crystallization, IX has mp 230–231°; λ_{max}^{KBr} 3.05, 3.10, 3.20 (NH), 5.77, 5.86 (C=N), 5.95 (C=O), and 6.65 μ (NH bend); λ_{max}^{EtOH} 235 mμ (ε 5040).

Anal. Calcd for $C_7H_6Cl_2F_4N_4O_2$: C, 25.9; H, 1.9; Cl, 21.9 F, 23.4. Found: C, 25.7; H, 2.2; Cl, 21.5; F, 22.7.

Preparation of Dichlorotetrafluoroacetone–Dicyandiamide (2:1) Adduct.—Dicyandiamide (8.4 g, 0.10 mole) was heated to 50° in 100 ml of acetonitrile. To this slurry was added 25 ml of dichlorotetrafluoroacetone so that the temperature rose to 80° and the solid completely dissolved. On cooling to 0°, 34.8 g of product was obtained: mp 274.5–275°. From the solvent another 2.0 g was obtained totaling 36.8 g (78%): λ_{max}^{KBr} 2.85, 3.05, 3.10, 3.26 (NH), 5.83, 5.90, 5.96 (C=O or C=N), 6.22, and 6.46 μ; λ_{max}^{EtOH} 214 mμ (ε 14,650).

Anal. Calcd for $C_8H_4Cl_4F_8N_4O_2$: C, 19.9; H, 0.8; Cl. 29.4; F, 31.5; N, 11.6; mol wt, 482. Found: C, 20.4; H, 1.0; Cl, 29.4; F, 31.6; N, 11.5; mol wt (cyroscopic in dimethyl sulfoxide), 449.

Derivatives of 1-Phenylazo-2-Naphthylamine. The Effect of Substituent on Color

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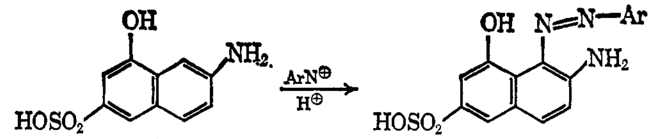
7-Amino-1-naphthyl acetate couples with diazonium salts at pH 4–5 only in the 8 position to give, after hydrolysis, pure 1-arylazo-2-amino-8-naphthols. An earlier observation that the color of these dyes is insensitive to acids and alkali, an effect presumably caused by strong hydrogen bonding with the azo group, has been confirmed. The visible absorption band centroids of these dyes are found to lie at 58 ± 2 mμ longer wavelengths than those of the corresponding 1-arylazo-2-naphthylamines and their values, for both dye systems bearing *meta* and *para* substituents on the phenylazo group, show good correlation with the Hammett and Taft σ values. The influence of substituents on color is examined.

Arylazo derivatives prepared from "γ acid" [7-amino-1-naphthol-3-sulfonic acid (1)] by coupling at the 8 position with diazonium salts in acid solution are well-established red to purple water-soluble dyes used commercially for color-fast dyeing of cotton.[3]



1

In 1951, Perekalin and Slabachevskaya[4] described the preparation of the parent azo dye free of the sulfonic acid group, 1-phenylazo-2-amino-8-naphthol (2),

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[3] See, for example, Colour Index No. 17020 ff, "Colour Index," 2nd ed, The Society of Dyers and Colourists, England, 1956; H. E. Woodward in "The Chemistry of Synthetic Dyes and Pigments," H. A. Lubs, Ed., Reinhold Publishing Corp., New York, N. Y., 1955, p 123 ff.

[4] V. V. Perekalin and N. M. Slabachevskaya, *J. Gen. Chem. USSR*, **21**, 985 (1951).