likely acetyl sulfide. Following attack at C-9, transacetylation can occur to give 7 and acetyl perchlorate. Solutions of the latter compound in acetic anhydride are well documented.⁸

Experimental Section

Melting points (Kofler apparatus) and boiling points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer, Model 237B spectrophotometer calibrated with a polystyrene film. Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Materials.—Acridine *N*-oxide,¹ acridone,⁴ and acetyl sulfide⁹ were prepared as previously described. Thioacridone was prepared by the method of Edinger and Arnold¹⁰ and chromatographed on alumina by elution with tetrahydrofuran. Thioacetic acid was refluxed over phosphorus pentoxide and distilled; the product was redistilled through a 24-in. spinning-band column: bp 86.0–86.4° (748 mm), n^{25} D 1.4620.

N-Acetoxyacridinium Perchlorate (6).—The general method of Muth and Darlak¹¹ was followed. A 0.5-ml aliquot of an ice-cold solution of 70% perchloric acid (1.3 g) in acetic anhydride (5 ml) was added dropwise to a stirred, ice-cold solution of 1 (0.15 g, 0.00076 mol) in acetic acid (1 ml) and acetic anhydride (2 ml). After 2 hr at 0°, reddish-brown crystals were collected under a nitrogen atmosphere, washed three times with cold anhydrous diethyl ether, and dried *in vacuo* over phosphorus pentoxide to give 0.060 g (33%) of 6: mp 186° dec; ir (KBr) 1821 cm⁻¹.

Anal. Calcd for $C_{18}H_{12}CINO_{6}$: C, 52.35; H, 3.58; N, 4.15. Found: C, 53.26; H, 3.72; N, 4.40. Tetra-n-butylammonium Thioacetate.—A 25% solution of

Tetra-*n*-butylammonium Thioacetate.—A 25% solution of tetra-*n*-butylammonium hydroxide in methanol was treated with a slight excess of thioacetic acid, concentrated on a rotary evaporator at reduced pressure, and refrigerated under an inert atmosphere. The residual oil crystallized and was dried *in vacuo* at 80° over phosphorus pentoxide to give a product (69%) of mp 74.6-77.6°.

Anal. Calcd for C₁₈H₃₉NOS: C, 68.08; H, 12.38; N, 4.41; S, 10.10. Found: C, 67.98; H, 12.49; N, 4.34; S, 10.26.

Product Identification.—A solution of 1 (0.10 g) in acetyl sulfide (50 ml) was allowed to remain at room temperature 16 hr and then evaporated to dryness at reduced pressure. The solid residue was chromatographed on alumina in tetrahydrofuran and recrystallized from methanol to give 0.064 g (58%) of 5, mp 259–261°; a mixture melting point showed no depression.

In another experiment a solution of 1 (33 mg) in acetyl sulfide (30 ml) was maintained at 15° for 40 hr, hydrolyzed with excess sodium hydroxide solution, and extracted with chloroform. The combined extract was washed with water and concentrated on a rotary evaporator to give a solid residue (35 mg) which by its ultraviolet visible spectrum (in acetonitrile) and by thin layer chromatography (in chloroform on alumina) was identical with thioacridone. By these same criteria, 1 was not present.

Rate Measurement.—Conductometric studies were carried out as previously described.⁴ At 15° the resistance of pure acetyl sulfide was 206,400 ohms, compared to 45,000 ohms for acetic anhydride.⁴

Spectrophotometric studies were conducted in a jacketed, 10-mm cell fitted with a Teflon stopper containing a glass probe thermistor, which was connected to a thermometric bridge and galvanometer. Water was circulated through the cell jacket from an external constant temperature bath; temperatures of the reaction solution were maintained at $48.95 \pm 0.05^{\circ}$. All apparatus was flushed with nitrogen and all transfers of solutions were conducted under a nitrogen atmosphere.

Registry No.—1, 10399-73-2; **6**, 25876-95-3; acetyl sulfide, 3232-39-1; tetra-*n*-butylammonium thioacetate, 25827-89-8.

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Novel Synthesis of a Dihydrotetrazapentalene from Trifluoroacetonitrile and Sodium Cyanide

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The carbon-to-nitrogen multiple bond in perfluoroalkyl imines and nitriles is extremely reactive in the addition of nucleophilic agents. Both hexafluoroacetone imine and trifluoroacetonitrile (4) combined with hydrogen cyanide under the influence of basic catalyst to give 1:1 adducts (1 and 2, respectively).^{1,2} Re-



cently, it was reported⁸ that 1 equiv of sodium cyanide reacts with 3 equiv of hexafluoroacetone imine to form a 1:3 adduct (3). This addition cannot be stopped at a 1:1 or a 1:2 adduct stage, presumably because these intermediate adducts are stronger nucleophiles than the cyanide ion.

We have found that trifluoroacetonitrile also reacts with sodium cyanide in a polar solvent to form a 1:3adduct. The structure of this adduct was determined to be a salt of a dihydrotetrazapentalene (9).



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The reaction is believed to proceed stepwise to give first the intermediate adduct 5, which adds to another nitrile unit to give 6. This intermediate (6) then cyclizes to give the 1:2 adduct 7 which adds still another nitrile unit to give intermediate 8. The final step is the cyclization of 8 to 9. This last step is unusual in that a nitrogen-to-nitrogen bond is formed by the addition of a nitrogen anion to a carbon-to-nitrogen double bond in a direction opposite to that normally observed. A driving force for this final step could be the formation of a resonance-stabilized salt (9), the anion of which is an aromatic structure. A 1:1 and 1:2 adduct of sodium cyanide with trifluoroacetonitrile (5 and 7) could not be isolated, presumably because these adducts are stronger nucleophiles than cyanide ion and react preferentially with the trifluoroacetonitrile.

This addition of sodium cyanide to 3 equiv of trifluoroacetonitrile closely parallels the known addition of potassium cyanide to 3 equiv of cyanogen to give an analogous dihydrotetrazapentalene that contains cyano groups in place of the trifluoromethyl groups.⁴

The dihydrotetrazapentalene structure of the anion of **9** was supported by the spectral data. The ¹⁹F nmr spectrum, which was obtained on the readily purified tetramethylammonium salt, indicated three different trifluoromethyl groups. The two lower field signals, probably due to the CF₃ groups at the 4 and 6 positions, were split to quartets by a spin-spin coupling of 2.1 The ultraviolet spectrum of the tetramethyl-Hz. ammonium salt showed maxima at 268 and 245 m μ , indicating aromaticity.

Acidification of the water-soluble sodium salt 9 gives a water-insoluble acidic product (10). Two tautomeric structures (10a and 10b) for this product are theoreti-



cally possible. Because of the acidic nature of $10 (pK_n)$ = 2.75 in 40% ethanol), the position of the lone hydrogen is difficult to ascertain. To determine which of the two tautomeric structures (10a and 10b) best represents 10, a sample containing a ¹⁵N label at the 3 position was prepared from ¹⁵N-labeled sodium cyanide and unlabeled trifluoroacetonitrile.

If the proton were bonded directly to the labeled nitrogen (as in 10b), a large spin-spin coupling between the ¹⁵N and ¹H would be expected in the proton nmr spectrum,⁵ unless hydrogen exchange were very rapid. Also, the signal band width should be much less than that observed in the spectrum of the unlabeled material, since ¹⁵N has no quadrupole.

The actual proton nmr spectrum of the labeled sample of 10 was essentially the same as that of the unlabeled sample in the temperature range from -120 to 30° . Since coupling to ¹⁵N was not observed, and signal narrowing due to loss of quadrupole interaction was not

observed, the proton is not tightly bound to the ¹⁵N. Rapid proton exchange (at least, in the nmr time scale) appears unlikely, since low temperatures, which should slow the exchange, did not change the width of the signal. Also, an equilibrating mixture containing appreciable amounts of both tautomers (10a and 10b) appears unlikely, since the ¹⁹F nmr spectrum of **10** in acetone shows well-resolved quartets for the two lower field absorptions. The evidence thus indicates that 10 exists primarily in only one tautomeric form, 10a, and that protonation of the anion of **9** occurs at the 1 position (on the unlabeled nitrogen).

When 10 was treated with diazomethane in ether, the crude methylated product apparently consisted of a 93:7 mixture of two isomeric monomethyl derivatives (11 and 12). The major product was purified by recrystallization. Its ¹⁹F and ¹H nmr spectra indicate that the protons on the methyl group are spin-spin coupled to the fluorines on two of the CF_3 groups (J_{FH} ~ 0.6 Hz). One of the coupled CF₃ groups is at the highest field position and is probably the group at the 2 position since it is not coupled to the other two CF_3 The other CF_3 group coupled to the methyl is groups. at the lowest field position, and is likely at the 4 position, since it has been observed that CF₃ groups attached to a carbon atom flanked by two nitrogen atoms absorb at a higher field position than CF₃ groups in otherwise similar situations attached to a carbon atom flanked by one nitrogen atom and one carbon atom⁶ If these assignments are correct, then it appears that the major methyl isomer is 11, since coupling of the methyl with the CF₃ groups at the 2 and 4 positions is more likely in this isomer than in structure 12.



Experimental Section

2.4.6-Tris(trifluoromethyl)-1,6a-dihydro-1,3,5,6a-tetrazapentalene (10).-Trifluoroacetonitrile, 85.5 g (0.9 mol), was distilled into stirred suspension of 25 g (0.5 mol) of sodium cyanide in 250 ml of dimethylformamide. The rate of addition was adjusted so that the temperature did not rise above 40°. The mixture was stirred for 1 hr and then poured into 300 ml of 10% hydrochloric acid. The oil that separated was washed with successive portions of water until it solidified. The solid was filtered off, washed with water, and dried in a desiccator over P₂O₅ to give 65.5 g (70%) of crude 10 as a light-yellow powder. A colorless sample, mp 180-195° dec, was obtained by recrystallization from benrule 100 100 uce, was obtained by following 200 (4250), and 228 (3750); ¹⁹F nmr (action), CCl₃F std, δ 59.8 ppm (q, J = 0.9(a, 50), τ mm (accorde), COAR stu, 5 55.5 ppm (q, J = 0.9 Hz, 3 F), 62.9 (q, J = 0.9 Hz, 3 F), and 64.9 (s, 3 F); ¹H mm (acctone) τ -3.3; ir (KBr) 6.00, 6.37, 6.53, and 6.66 μ . Anal. Calcd for C₁HF₉N₄: C, 26.94; H, 0.32; F, 54.79; N, 17.95; neut equiv, 312. Found: C, 27.07; H, 0.36; F, 54.89.

54.86; N, 17.69; neut equiv, 312.

Tetramethylammonium Salt of 10.-A solution of 1.0 g of tetramethylammonium chloride in 10 ml of water was mixed with a solution prepared by dissolving 1.0 g of 10 in 10 ml of 5% sodium bicarbonate. The precipitate that formed was filtered off, washed with water, and recrystallized from alcoholether to give 0.6 g of the tetramethylammonium salt of 10 as colorless crystals: mp 284-285° dec; uv (ethanol) λ_{max} 268 mµ

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Notes

(ϵ 7100) and 245 (5800); ir (KBr) 6.28, 6.55, 6.69 μ ; ¹H nmr (acetone- d_{θ}) τ 6.53 (t, $J_{\rm NH} = 0.5$ Hz); ¹⁹F nmr (acetone), CCl₈F std, δ 57.2 ppm (q, J = 2.1 Hz, 3 F), 60.9 (q, J = 2.1 Hz, 3 F), and 64.2 (s, 3 F). An analytical sample was prepared by a second recrystallization from alcohol-ether.

Anal. Calcd for $C_{11}H_{12}F_{9}N_{5}$: C, 34.29; H, 3.14; F, 44.39; N, 18.18. Found: C, 34.41; H, 3.30; F, 44.14; N, 17.84.

3-Methyl-2,4,6-tris(trifluoromethyl)-3,6a-dihydro-1,3,5,6a-tetrazapentalene (11).—A 3% solution of diazomethane in ether was added dropwise to a solution of 1.0 g of 10 in 5 ml of ether until no further evolution of nitrogen was evident. The solution was evaporated to dryness. The ¹H nmr spectrum of the crude product showed two signals at 5.65 (7%) and 6.08 (93%). Two recrystallizations from pentane gave 0.75 g of 11 as long needles: mp 43-45.5°; uv (ethanol) λ_{max} 266 m μ (ϵ 3800), 226 (5500); ir (KBr) 6.12, 6.42, 6.49, and 6.63 μ ; ¹H nmr (acetone- d_b) τ 6.08 (poorly resolved multiplet, probably two overlapping quartets, $J_{\rm HF} \sim 0.6$ Hz); ¹⁰F nmr (acetone), CCl₈F std, δ 57.5 ppm (m, probably two overlapping quartets with $J_{\rm FF}$ = 1.0 and $J_{\rm FH}$ = 0.6 Hz), 62.2 (q, J = 1.0 Hz), and 64.1 (q, J = 0.6 Hz). An analytical sample was prepared by a third recrystallization from pentane.

Anal. Caled for C₈H₈F₉N₄: C, 29.46; H, 0.93; F, 52.43; N, 17.18. Found: C, 29.26; H, 0.87; F, 52.48; N, 16.90.

Registry No.—10a, 25894-19-3; tetramethylammonium salt of 10a, 25894-20-6; 11, 25894-21-7.

Structures of Alleged 1,4-Dihydropyrazines

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The 1,4-dihydropyrazine ring system is an interesting conjugated cyclic structure containing 8 π electrons. It is electronically analogous to cyclooctatetraene and 1*H*-azepine, both of which have in recent years displayed some fascinating chemistry.¹ Since the 1,4-



dihydropyrazine ring system is generally thought to be a known structure² and has been used to demonstrate the nonaromatic character of $8-\pi$ -electron compounds³ we are prompted to report the following results. We have repeated the work in the most frequently quoted reference⁴ and find the original structural assignments to be in error.

Mason⁴ has reported that the base-catalyzed cyclo-

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dehydration of N-phenacylbenzylamine hydrobromide (4) gives 1,4-dihydropyrazine (5). The nmr spectrum



of the product from this reaction showed in the nonaromatic region two doublets at τ 5.17 and 5.30 (1 H, J = 5.0 Hz), a quartet (AB), centered at 6.15 (2 H, J = 15.0 Hz), and a complex multiplet at 6.83-7.62(2 H). This spectrum is clearly inconsistent with 5. However, structure $\mathbf{6}$ is in agreement with the available data. The two proton multiplet at τ 6.83-7.62 and the one proton doublets at 5.17 and 5.30 are assigned to the AB and the X portions of an ABX spectrum. These absorptions represent the benzyl hydrogens of the benzyl group at C_6 and methine hydrogen at C_6 . Irradiation of the τ 6.83-7.62 multiplet caused the doublets at 5.17 and 5.30 to collapse into a singlet confirming the coupling between these two groups of hydrogens. The AB quartet centered at τ 6.15 is assigned to the benzyl hydrogens adjacent to the nitrogen atom. The nonequivalence of the hydrogens on both benzyl substituents is attributable to the presence of the asymmetric carbon atom (C_6) in dihydropyrazine 6. Similar effects have been observed in related systems.⁵

Pyrolysis of 6 gave a mixture of pyrazines which further supports the postulated dihydropyrazine structure for 6.



The reaction of diphenacylbenzylamine hydrobromide with benzylamine is also reported to give the 1,4dihydropyrazine ring system,⁴ 7. The nmr spectrum of the reaction product, which is similar to 6, is inconsistent with structure 7. The methine hydrogen at C₆ occurs as two doublets (τ 5.17 and 5.32, J = 5 Hz) further split by the vinyl hydrogen (τ 3.42, d, J = 1Hz) at C₂. The benzyl hydrogens of the benzyl group (τ 6.87-7.70) at C₆ occur as a complex multiplet. Irradiation of the τ 6.87-7.70 multiplet caused the doublets at τ 5.17-5.32 to collapse into a singlet thus confirming the coupling between these groups of hydrogens. The benzyl hydrogens adjacent to the nitrogen occur as an AB quartet centered at τ 6.32 (J = 15 Hz).

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