

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

### 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,<sup>1</sup> acridone,<sup>4</sup> and acetyl sulfide<sup>9</sup> were prepared as previously described. Thioacridone was prepared by the method of Edinger and Arnold<sup>10</sup> 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),  $n_D^{20}$  1.4620.

***N*-Acetoxyacridinium Perchlorate (6).**—The general method of Muth and Darlak<sup>11</sup> 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  $\text{cm}^{-1}$ .

*Anal.* Calcd for  $\text{C}_{15}\text{H}_{12}\text{ClNO}_6$ : 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 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  $\text{C}_{18}\text{H}_{39}\text{NOS}$ : 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.<sup>4</sup> At 15° the resistance of pure acetyl sulfide was 206,400 ohms, compared to 45,000 ohms for acetic anhydride.<sup>4</sup>

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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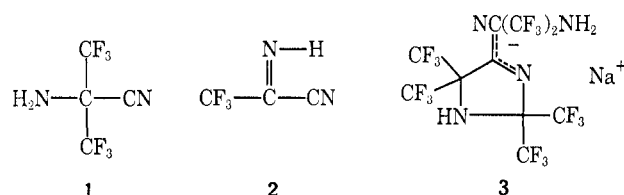
### Novel Synthesis of a Dihydropentazapentalene from Trifluoroacetonitrile and Sodium Cyanide

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Contribution No. 1680 from the Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

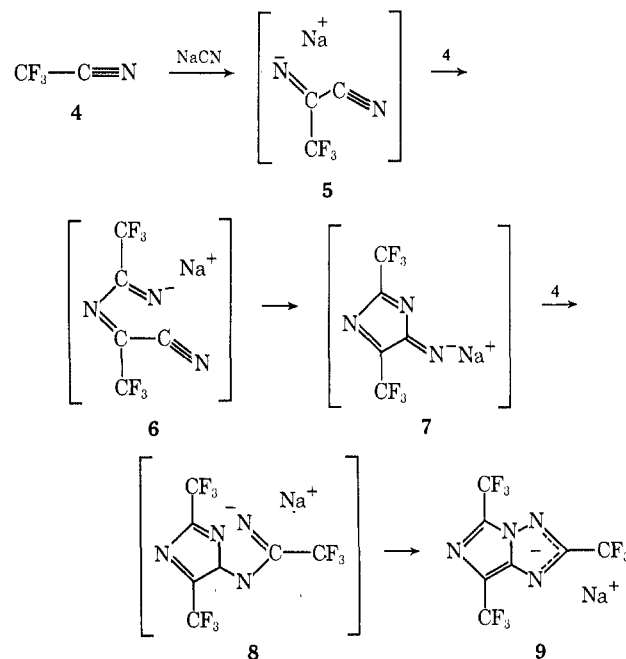
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The carbon-to-nitrogen multiple bond in perfluoroalkyl imines and nitriles is extremely reactive in the addition of nucleophilic agents. Both hexafluoroacetone imine and trifluoroacetonitrile (4) combined with hydrogen cyanide under the influence of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



cently, it was reported<sup>3</sup> 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 1:3 adduct. The structure of this adduct was determined to be a salt of a dihydropentazapentalene (9).



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( $\epsilon$  7100) and 245 (5800); ir (KBr) 6.28, 6.55, 6.69  $\mu$ ;  $^1\text{H}$  nmr (acetone- $d_6$ )  $\tau$  6.53 (t,  $J_{\text{NH}} = 0.5$  Hz);  $^{19}\text{F}$  nmr (acetone),  $\text{CCl}_3\text{F}$  std,  $\delta$  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  $\text{C}_{11}\text{H}_{12}\text{F}_3\text{N}_2$ : 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  $^1\text{H}$  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)  $\lambda_{\text{max}}$  266 m $\mu$  ( $\epsilon$  3800), 226 (5500); ir (KBr) 6.12, 6.42, 6.49, and 6.63  $\mu$ ;  $^1\text{H}$  nmr (acetone- $d_6$ )  $\tau$  6.08 (poorly resolved multiplet, probably two overlapping quartets,  $J_{\text{HF}} \sim 0.6$  Hz);  $^{19}\text{F}$  nmr (acetone),  $\text{CCl}_3\text{F}$  std,  $\delta$  57.5 ppm (m, probably two overlapping quartets with  $J_{\text{FF}} = 1.0$  and  $J_{\text{FH}} = 0.6$  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.* Calcd for  $\text{C}_9\text{H}_3\text{F}_3\text{N}_4$ : 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.

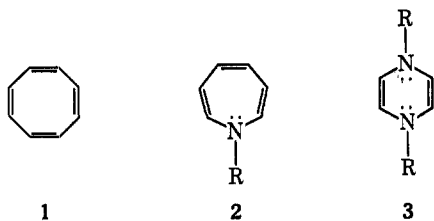
## Structures of Alleged 1,4-Dihydropyrazines

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



dihydropyrazine ring system is generally thought to be a known structure<sup>2</sup> and has been used to demonstrate the nonaromatic character of 8- $\pi$ -electron compounds<sup>3</sup> we are prompted to report the following results. We have repeated the work in the most frequently quoted reference<sup>4</sup> and find the original structural assignments to be in error.

Mason<sup>4</sup> has reported that the base-catalyzed cyclo-

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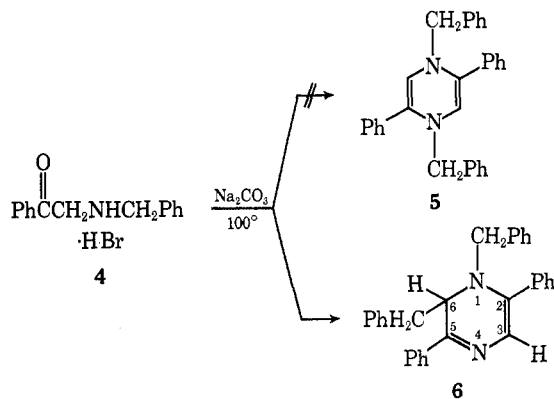
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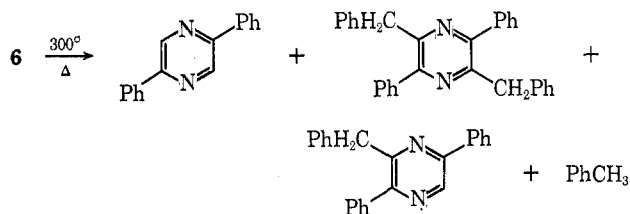
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dehydration of *N*-phenacylbenzylamine hydrobromide (4) gives 1,4-dihydropyrazine (5). The nmr spectrum



of the product from this reaction showed in the non-aromatic region two doublets at  $\tau$  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 6 is in agreement with the available data. The two proton multiplet at  $\tau$  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<sub>6</sub> and methine hydrogen at C<sub>6</sub>. Irradiation of the  $\tau$  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  $\tau$  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<sub>6</sub>) in dihydropyrazine 6. Similar effects have been observed in related systems.<sup>5</sup>

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 1,4-dihydropyrazine ring system,<sup>4</sup> 7. The nmr spectrum of the reaction product, which is similar to 6, is inconsistent with structure 7. The methine hydrogen at C<sub>6</sub> occurs as two doublets ( $\tau$  5.17 and 5.32,  $J = 5$  Hz) further split by the vinyl hydrogen ( $\tau$  3.42, d,  $J = 1$  Hz) at C<sub>2</sub>. The benzyl hydrogens of the benzyl group ( $\tau$  6.87–7.70) at C<sub>6</sub> occur as a complex multiplet. Irradiation of the  $\tau$  6.87–7.70 multiplet caused the doublets at  $\tau$  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  $\tau$  6.32 ( $J = 15$  Hz).

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