TABLE I

EFFECT OF STRUCTURE ON CO REACTION PRODUCTS

Nitro compd	Products[a] (yield, %)	
1a	3 (39)	2a (24)
1b	3 (30)	2b (52)
1c	3 (18)	
2-Nitrobutane	3 (89)	2-Butanone[b] (58)
Nitrocyclohexane	3 (37)	N-Cyclohexylurethan (trace)
2-Methyl-2-nitropropane	Recovered unchanged	

[a] Significant quantities of volatile by-products such as ammonia are formed in most of these reactions. [b] Isolated as the 2,4-dinitrophenylhydrazone.

unchanged after being subjected to the reaction conditions.

Ethanol is the preferred solvent for this reaction, but benzene has been employed successfully (reaction is much slower in benzene). Temperatures have been varied from 125 to 200° and pressures from 2000 to 5000 psig with no significant changes in product distributions. Rhodium is equally as effective as palladium for the noble metal portion of the catalyst while carbon or alumina supports appear to be equivalent. All the components of the reaction system (noble metal, ferric chloride, and carbon monoxide) were found to be necessary; if any one is omitted, none of the pyridine product is observed.

Falbe[3] has reported that n-butyraldoxime reacts with 1:1 hydrogen–carbon monoxide in the presence of a cobalt carbonyl catalyst to yield **2a** (24%) and butyramide (38%). Treatment of this oxime under our conditions also gave **2a** (33%) suggesting that oxime intermediates may be involved in the pyridine formation. The 2-butanone isolated from the reaction of 2-nitrobutane could be derived from the corresponding oxime.

These results as well as those previously reported[1–3,5] suggest that nitro compounds can react with carbon monoxide to yield a number of different products depending on catalyst and solvent as well as the structure of the nitro compounds.

Experimental Section[6]

2-Propyl-3,5-diethylpyridine (2a).—Into a glass-lined autoclave were charged 16.9 g (0.162 mol) of 1-nitrobutane, 2.11 g (0.013 mol) of anhydrous ferric chloride, 4.2 g of 5% palladium on carbon,[7] and 100 ml of anhydrous ethanol. The autoclave was pressurized to 5,000 psig with carbon monoxide[8] and heated for 2 hr at 190°. After cooling and venting, the product mixture was filtered to remove the catalyst. Analysis of the filtrate (vpc, silicone rubber column) indicated **2a** and **3** were present in approximately equal amounts. After evaporation of the solvent, the products were distilled, bp 45–70° (0.1 mm), affording 12.3 g of a solid-liquid mixture. Washing of this mixture with petroleum ether left 5.7 g (39%) of **3**, which after purification melted at 46–48° and was identical with that of an authentic sample (vpc, ir, mixture melting point). The pyridine **2a**, 2.3 g (24%), was recovered from the washings by evaporation and acid extraction. The amine was further purified by preparative vpc: uv max (C₂H₅OH), 270 mμ (ε 4400), (HCl, C₂H₅OH), 277 (1800); nmr (CDCl₃) δ 8.28 (d, 1, J = 2 Hz, py-H), 7.28 (d, 1, J = 2 Hz, py-H), 2.65 (m, 6, py-CH₂–), 1.75 (m, 3, –CH₂—CH₂—CH₃), and 1.20–0.99 ppm (overlapping t, 9,

(6) Melting points were determined on a Mel-Temp block and are uncorrected. Vpc, nmr, uv, and mass spectral measurements were carried out on an F & M Model 500 chromatograph, a Varian A-60, a Beckman DU and a CEC Model 110, respectively.

(7) Obtained from Engelhard Industries in the unreduced form and dried at 350° under nitrogen just prior to use.

(8) Obtained from Air Products and Chemicals, Inc., CP grade.

–CH₃); mass spectrum (70 eV) m/e 177 (M), 162, 148, 134, 129, 91; picrate mp 121–122° (lit.[9] mp 122°).

Anal. Calcd for C₁₃H₂₂N₄O₇: C, 53.20; H, 5.46; N, 13.79. Found: C, 53.18; H, 5.52; N, 13.84.

The nmr spectrum of **2a** was identical with the spectrum of the authentic material.[3]

n-Butyraldoxime was substituted for **1a** in the above experiment and **2a** was isolated in 33% yield. No **3** was evident in the product mixture, but the ir spectrum of the ethanol solution showed a strong absorption band at about 2000 cm⁻¹ suggesting the presence of iron pentacarbonyl.

2-Ethyl-3,5-dimethylpyridine (2b).—1-Nitropropane was treated with carbon monoxide under the conditions described above for **1a**. The yield of **3** was 30% and **2b**, 52%. The structure of **2b** was established from the following data: uv max (C₂H₅OH) 270 mμ (ε 3400), (HCl, C₂H₅OH), 274 (5800); nmr (CDCl₃) δ 8.19 (broad s, 1, py-H), 7.20 (broad s, 1, py-H), 2.76 (q, 2, J = 7 Hz, py-CH₂CH₃), 2.23 (s, 6, py-CH₃), and 1.25 ppm (t, 3, J = 8 Hz, CH₂-CH₃); mass spectrum (70 eV) m/e 135 (M), 134, 120, 107, 91, 79, 77; picrate mp 154–155° (lit.[10] mp 156–157°).

Anal. Calcd for C₁₅H₁₆N₄O₇: C, 49.45; H, 4.43; N, 15.38. Found: C, 49.20; H, 4.18; N, 15.42.

The nmr spectrum of **2b** was identical with the spectrum of the authentic material.[3]

(9) T. M. Patrick, *J. Amer. Chem. Soc.*, **74**, 2984 (1952).

(10) A. E. Chichibabin and M. P. Oparina, *J. Prakt. Chem.*, **107**, 146 (1924).

Rearrangement of Aromatic N-Oxides. IV. The Reaction of Acridine N-Oxide with Acetyl Sulfide[1]

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Previous reports from this laboratory have involved mechanistic studies of the rearrangement of aromatic N-oxides in acetic anhydride.[3] From a detailed kinetic analysis of such a reaction with acridine N-oxide (1), it was concluded that the key step involved an intramolecular rearrangement of the N-acetoxyacridinium ion (2).[4] This was somewhat surprising since in the analogous reaction with pyridine N-oxide (3) kinetic[5] and oxygen-18[6] studies established that the pathway

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(1) Part III: J. H. Markgraf and C. G. Carson, III, *J. Org. Chem.*, **29**, 2806 (1964).

(2) Based on the Honors theses, Williams College, of M.-K. Ahn, 1963, C. G. Carson, III, 1964, and G. A. Lee, 1967.

(3) For general reviews, see (a) E. Ochiai, "Aromatic N-Oxides," Elsevier, Amsterdam, 1967, pp 290–302, 310–325; (b) V. J. Traynelis, "Mechanisms of Molecular Migration," Vol. 2, B. S. Thyagarajin, Ed., Wiley-Interscience, New York, N. Y., 1969, Chapter 1.

(4) J. H. Markgraf and M.-K. Ahn, *J. Amer. Chem. Soc.*, **86**, 2699 (1964).

(5) J. H. Markgraf, H. B. Brown, Jr., S. C. Mohr, and R. G. Peterson, *ibid.*, **85**, 958 (1963).

(6) S. Oae and S. Kozuka, *Tetrahedron*, **21**, 1971 (1965).

was intermolecular. These data, therefore, corresponded to the correlation that rearrangement of **3** proceeded to the α position *via* an intermolecular process while **1** was converted to the γ derivative *via* an intramolecular process. In order to corroborate our mechanistic inferences from the kinetic study, we directed our attention to the reaction of **1** with the corresponding thioanhydride, acetyl sulfide (Ac_2S). On the assumption that the reactants initially generate **2** and thioacetate ions, alternate pathways can subsequently afford either acridone (**4**) or thioacridone (**5**) *via* intra- or intermolecular processes, respectively. Although the comparison of the thioanhydride with acetic anhydride introduced a more competitive nucleophile (thioacetate *vs.* acetate), it was felt that a combined product–kinetic investigation would offer additional insight into this rearrangement. No previous studies have included thioanhydrides; our work was in progress when the reaction of **1** with oxygen-18 labeled acetic anhydride was reported.[7] The latter study confirmed the intramolecularity of the rearrangement.

Results and Discussion

The development of a suitable analytical scheme proved more difficult than anticipated. The previous techniques of spectrophotometric[4,5] and conductometric[4] methods were unsatisfactory in the present case: the slower rate of hydrolysis of Ac_2S introduced inaccuracies in the quenching of aliquots and the variation of resistance with time showed only a further slight decrease during the course of the reaction (following the initial large change upon addition of **1**). The process finally used involved monitoring the ultraviolet visible spectrum of a solution of **1** in a thermostated cell.
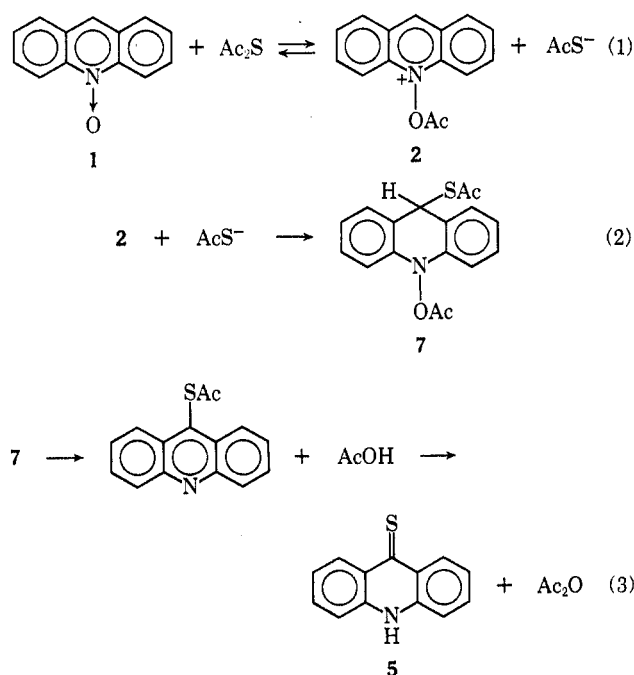
The results of such runs were quite different from those of the earlier studies in acetic anhydride (Ac_2O). The product was not acridone (**4**, λ_{max} 392 mμ), but thioacridone (**5**, λ_{max} 481 mμ). It was established by control experiments that **4** was completely stable in Ac_2S and was not converted to **5**. Unfortunately, **5** was not indefinitely stable in the reaction medium and the initial increase in absorbance at 481 mμ was accompanied by a slow decrease. The rearrangement of **1** in Ac_2S was considerably slower than in Ac_2O and, over the longer time periods required, the complex variation in the absorbance at 481 mμ rendered quantitative kinetic data unreliable. The spectrum of the initial solution of **1** in Ac_2S, however, exhibited absorbance at 367 mμ which decreased with time. This peak undoubtedly corresponded to species **2**, since the identical spectrum was observed for a solution of *N*-acetoxyacridinium perchlorate (**6**) in Ac_2S. Observation of this peak in a run that was initially 3.84 × 10^{-4} *M* **1** in Ac_2S at 49.0° indicated 11% rearrangement after 5.5 hr. This reaction rate was strikingly slower than the half-life of 0.3 hr for **1** in Ac_2O at 25°.

The rearrangement of acridine *N*-oxide in acetyl sulfide produced thioacridone. This fact established that an intermolecular pathway was operative. Our original objective would have required at this point determination of the thermodynamic activation param-

eters. By such data the intermolecular process for the 1–Ac_2S system could then have been contrasted with the intramolecular process for the 1–Ac_2O system. The results of Oae's study of oxygen-18 labeling appeared during this time,[7] and further attempts to obtain quantitative kinetic data were abandoned.

There still existed the opportunity to test the presumed intermediacy of the *N*-acetoxyacridinium ion (**2**) and attention was focused on that species. Preparation of the previously unknown salt **6** was accomplished and its above-mentioned spectrum confirmed that a solution of **1** in Ac_2S rapidly generated **2**. A kinetic run of **6** (3.67 × 10^{-4} *M*) in Ac_2S at 49.0° indicated 40% rearrangement after only 3.0 hr. Identical runs to which were added trace amounts of thioacetic acid or tetra-*n*-butylammonium thioacetate showed further enhancement of the rate of appearance of **5**.

All of these data are consistent with the following mechanistic scheme. Establishment of an initial

$$2 \;+\; AcS^- \;\longrightarrow\;\text{(structure 7)} \qquad (2)$$

$$7 \;\longrightarrow\;\text{(structure)} \;+\; AcOH \;\longrightarrow\;\text{(structure 5)} \;+\; Ac_2O \qquad (3)$$

equilibrium (eq 1) in such systems is well documented.[3] The rate-determining step is considered to be the intermolecular attack by thioacetate ion at C-9 to give **7** (eq 2). Subsequent loss of acetic acid with concomitant aromatization followed by transacetylation to give thioacridone and acetic anhydride (eq 3) are inferred to be rapid and irreversible from the analogous steps observed in the 1–Ac_2O system.[4] The generation of Ac_2O during the course of the rearrangement accounts for the observed conductometric behavior. The failure to detect acridone vitiates any intramolecular process, a pathway known to occur in acetic anhydride. The present observations with acetyl sulfide, therefore, are consistent with a change in mechanism. This result can be attributed to the enhanced nucleophilicity of thioacetate.

The facile conversion of **6** to **5** in Ac_2S without added thioacetate species was unexpected. This reaction corresponds formally to eq 4. The nucleophile is most

(7) S. Oae, S. Kozuka, Y. Sakaguchi, and K. Hiramatsu, *Tetrahedron.*, **22**, 3143 (1966).

$$6 \;+\; Ac_2S \;\longrightarrow\; 5 \;+\; Ac_2O \;+\; AcClO_4 \qquad (4)$$
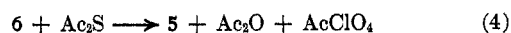
likely acetyl sulfide. Following attack at C-9, trans-acetylation can occur to give 7 and acetyl perchlorate. Solutions of the latter compound in acetic anhydride are well documented.[8]

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 sulfide[9] were prepared as previously described. Thioacridone was prepared by the method of Edinger and Arnold[10] 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 Darlak[11] 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 $C_{15}H_{12}ClNO_6$: 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 $C_{18}H_{39}NOS$: 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.[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 ± 0.05°. 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.

(8) (a) H. Burton and P. F. G. Praill, *J. Chem. Soc.*, 2034 (1950). (b) G. Jander and H. Surawski, *Z. Electrochem.*, **65**, 469 (1961). (c) G. N. Dorofeenko, Z. N. Nazarova, and V. N. Novikov, *Zh. Obshch. Khim*, **34**, 3918 (1964); *Chem. Abstr.*, **62**, 9099c (1965).
(9) J. H. Markgraf, G. A. Lee, and J. F. Skinner, *J. Phys. Chem.*, **72**, 2276 (1968).
(10) A. Edinger and W. Arnold, *J. Prakt. Chem.*, **64**, 182 (1901).
(11) C. W. Muth and R. S. Darlak, *J. Org. Chem.*, **30**, 1909 (1965).
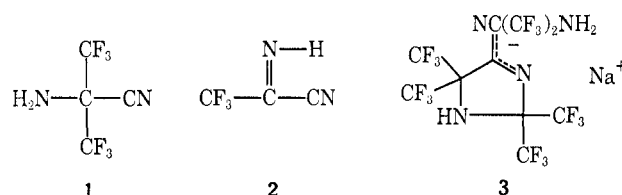

Novel Synthesis of a Dihydrotetrazapentalene from Trifluoroacetonitrile and Sodium Cyanide

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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 reported[3] 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 dihydrotetrazapentalene (9).
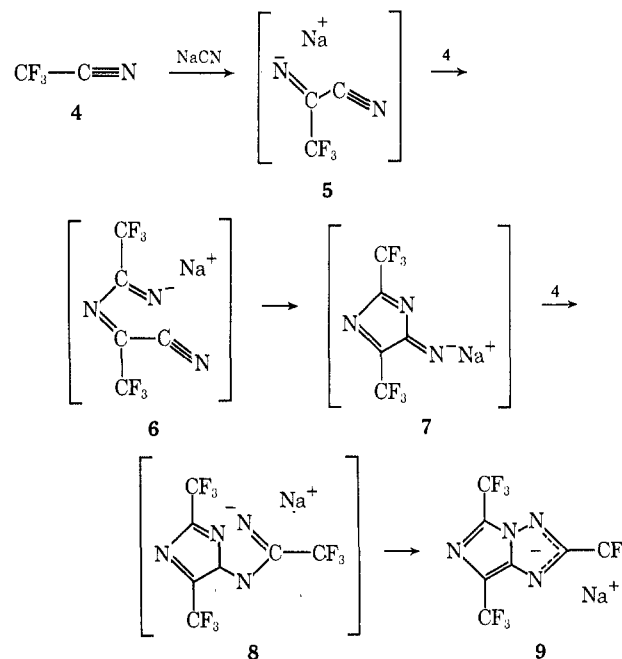
(1) W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).
(2) W. J. Middleton and C. G. Krespan, *ibid.*, **33**, 3625 (1968).
(3) W. J. Middleton and C. G. Krespan, *ibid.*, **35**, 1480 (1970).