TABLE I

SPECTRAL PROPERTIES OF N-ALKYL-N-FLUOROCARBAMYL FLUORIDES

Compd	ν_{COF}, μ	$\delta_{\alpha\text{-CH}}$, ppm	J_{FH}, cps	J_{FF}, cps	ϕ_{NF}, ppm	ϕ_{CF}, ppm
$CH_3CH_2N(F)C(=O)F$	5.4, 5.5	3.83	30	44	+71.4	+18.9
$CH_3CH_2CH_2N(F)C(=O)F$	5.4, 5.5	3.76	31	44	+69.4	+20.0
$CH_3CH_2CH_2CH_2N(F)C(=O)F$	5.37, 5.48	....	28	56	+69.3	+20.7

of III, the major product, contained a sharp doublet centered at ϕ +20 (J_{FF} = 44 cps) which is assigned the carbonyl fluorine atom. The coupling constant is not unreasonable for coupling through the carbonyl to a single fluorine on the nitrogen. The NF absorption appears as two overlapping triplets centered at ϕ +69.4. The major coupling (J_{FF} = 44 cps) of the NF signal is caused by the fluorine–fluorine coupling whereas the minor splitting ($J_{FH} \sim 30$ cps) is due to two equivalent adjacent protons in the side chain. By spin decoupling the protons, the nitrogen-bound fluorine signal can be reduced from a double triplet to a doublet and no further.

The proton nmr is also consistent in that the methylene protons adjacent to the nitrogen appear as a pair of triplets centered at δ 3.75. The major (~30 cps) and minor (7 cps) coupling allow assignment to the methylene protons next to the nitrogen bearing a single fluorine atom. The remaining spectral features are those of the ethyl group which remained intact.

The spectral details of the remaining side products are outlined briefly in the Experimental Section. The fluorine spectra of all carbamyl fluorides were virtually identical in each case as listed in Table I above.

The successful fluorination of the carbamyl fluoride (IV) demanded extension to the carbamyl chloride as the latter is more cleanly prepared. *n*-Propylcarbamyl chloride (V) was formed from the isocyanate in the fluorination solution directly by adding 1 equiv of anhydrous HCl. This solution was fluorinated at −78° in the presence of sodium fluoride to produce a high yield of N-propyl-N-fluorocarbamyl chloride (VI). Trace amounts of propyl isocyanate were formed as a by-product.

$$F_2 + \underset{\text{V}}{CH_3CH_2CH_2N(H)C(=O)Cl} \longrightarrow \underset{\text{VI}}{CH_3CH_2CH_2N(F)C(=O)Cl} + HF$$

Compound VI was identified by its nmr spectrum in that the methylene protons adjacent to the nitrogen atom are shifted to δ 3.86 (*cf.* Table I, δ_{av} 3.79 carbamyl fluoride) and exhibit the characteristic coupling constant of 31 cps. The fluorine nmr exhibited the expected signal at ϕ +46.2 as a triplet (J_{FH} = 31 cps).

The carbamyl chloride is difficult to purify because of limited heat stability but was converted to the phenylurea derivative (VII) with aniline. The spectral and analytical results of derivative VII along with the isolation of aniline hydrochloride are in accord with the postulated structure.

$$CH_2CH_2CH_2N(F)C(=O)Cl + C_6H_5NH_2 \longrightarrow \underset{\text{VII}}{CH_3CH_2CH_2N(F)C(=O)NHC_6H_5}$$

Summary.—The fluorination of the CN double bonds of alkyl isocyanates does not involve direct addition but rather side-chain fluorination followed by substitution on nitrogen of the carbamyl fluoride by-product. Direct, low-temperature fluorination of carbamyl fluorides or chlorides provides a convenient synthetic procedure for N-fluorocarbamyl halides. Such halides are useful precursors to other N-fluoroureas and carbamates.

Registry No.—I, 10074-87-0; II, 10074-88-1; III, 10074-89-2; IV, 10074-90-5; *n*-propyl-N-fluorocarbamyl chloride, 10074-91-6; VII, 10074-92-7; N-ethyl-N-fluorocarbamyl fluoride, 10074-93-8; N-butyl-N-fluorocarbamyl fluoride, 10074-94-9.

Acknowledgment.—This work was sponsored under Army Ordnance Contract DA-01-021 ORD-11878. We are grateful to Mr. Morris Howard for technical assistance and to Mrs. Carolyn Haney for infrared and nmr spectra.

Some Reactions of the 4-(α,α-Dicyanomethylene) Derivatives of 1,2,3,4-Tetrahydroquinoline, 1-Methyl-1,4-dihydroquinoline, and 1-Methyl-6-methoxy-1,4-dihydroquinoline[1]

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University of Colorado, Boulder, Colorado

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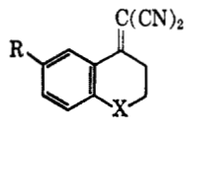
It has been shown by Campaigne and co-workers[2,3] that the treatment of α-tetrylidenemalononitrile (1) and 6-methylthiochroman-4-ylidene malononitrile (2) with concentrated sulfuric acid produced the cyclized

(1) This work was supported by a Continental Oil Co. Fellowship and a Public Health Service Research Grant CA 02997-08 from the National Cancer Institute, National Institutes of Health.

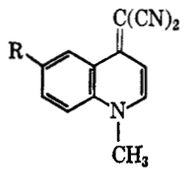
(2) E. Campaigne, G. Bulbenko, W. Kreighbaum, and D. Maulding, *J. Org. Chem.*, **27**, 4428 (1962).

(3) E. Campaigne and C. DeWitt Blanton, Jr., *Tetrahedron Letters*, No. 36, 2489 (1964).

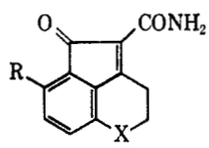
products, 2-carbamyl-3,4-trimethylene-1-indenone (**3**), and 4-carbamyl-2,3-dihydro-6-methyl-5H-cyclopenta-[*d*,*e*]benzothiopyran-5-one (**4**), respectively.



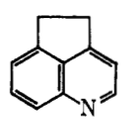
1, X = CH_2; R = H
2, X = S; R = CH_3
5, X = NH; R = H



6, R = H
7, R = OCH_3



3, X = CH_2; R = H
4, X = S; R = CH_3



8

It was considered worth-while to attempt similar ring closure reactions with 4-(α,α-dicyanomethylene)-1,2,3,4-tetrahydroquinoline (**5**), 1-methyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline (**6**), and 1-methyl-4-(α,α-dicyanomethylene)-6-methoxy-1,4-dihydroquinoline (**7**) in an attempt to form substances containing an acequinoline nucleus **8**. Although the desired ring closure was not achieved, these substances exhibited some interesting transformations which are described in this paper.

The condensation of 4-keto-1,2,3,4-tetrahydroquinoline[4] with malononitrile[5] produced the bright orange 4-(α,α-dicyanomethylene)-1,2,3,4-tetrahydroquinoline (**5**). With concentrated sulfuric acid this substance gave a white compound which analyzed for $C_{12}H_{11}N_3O_2$, and which had ultraviolet bands at 286 mμ (ϵ 4700), 303 (4000) and 318 (3400). The infrared spectrum showed two amide NH_2 bands at 3400 and 3200 cm^{-1} and two carbonyl bands at 1690 and 1660 cm^{-1}. These data were interpreted to indicate the formation of 4-quinolylmalonamide[6] (**10**) rather than a derivative of acequinoline.

Undoubtedly the initial product in the sulfuric acid hydrolysis of **5** is the 1,2-dihydro derivative, which then must undergo dehydrogenation to give **10**. This would most likely occur by air oxidation or disproportionation. The latter is ruled out by the fact that **10** was recovered in 80% yield. Johnson and Buell[7] have shown that 1,2-dihydroquinoline is completely transformed to quinoline upon exposure to air for two days. The extensive extraction period (>3 days) required to recover our product provides ample opportunity for air oxidation. Furthermore, the extinction coefficient (1520)[7] for the 278-mμ absorption band of 1,2-dihydroquinoline is somewhat lower than that of the 286-mμ band of **10**. If **10** is a quinoline derivative its ultraviolet spectrum should closely approximate that of lepidine,[8] $\lambda_{max}^{95\%\ alcohol}$ 280 mμ (ϵ 4750), $\lambda_{max}^{10\%\ alcohol}$ 313 mμ (ϵ 2730). That this is the case is quite clear.

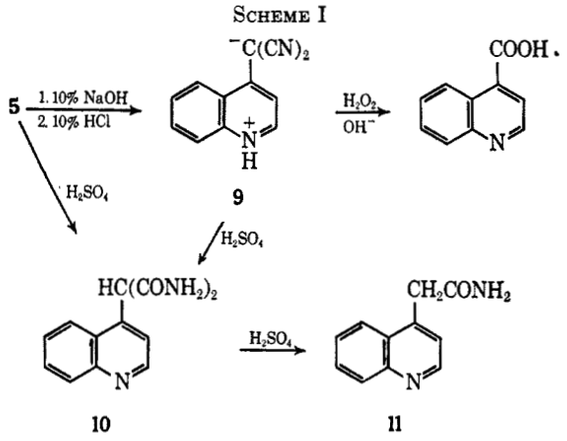
Finally, the nuclear magnetic resonance (nmr) spectrum of **10** in trifluoroacetic acid showed only one signal (singlet at 5.73 ppm) up field from the aromatic region and this was assigned to the dicarbamylmethyl proton.

Refluxing **5** with 10% aqueous sodium hydroxide produced a yellow solution from which two substances were isolated. One product proved to be 4-keto-1,2,3,4-tetrahydroquinoline which undoubtedly arose by reversal of the condensation used in preparing **5**. This process accounted for the fate of >50% of the starting material.

The other and more interesting product was a yellow, high melting (mp 330°) compound (**9**) which separated when 10% hydrochloric acid was added to the solution. Analysis of this product indicated the empirical formula $C_{12}H_7N_3$ and molecular weight determinations agreed well with this formula. The infrared spectrum showed NH absorptions at 3250 and 3130 cm^{-1}, strong amine salt absorption at 1600 cm^{-1}, and two nitrile bands at 2200 and 2179 cm^{-1}. The ultraviolet spectrum of **9**, with absorption at 270 mμ (ϵ 7000) and 280 mμ (ϵ 6500) and strong chromophores at 400 mμ (ϵ 20,000) and 418 mμ (ϵ 25,000) indicated a quinoline nucleus. A nmr spectrum in trifluoroacetic acid showed only aromatic hydrogens.

Formation of the quinoline nucleus from **5** (Scheme I) requires oxidation. Considering the fact that

SCHEME I



>50% of **5** was converted to 4-keto-1,2,3,4-tetrahydroquinoline, the quantity of **5** remaining was converted to **9** in 76% yield. This indicates that aromatization is due to air oxidation rather than disproportionation. An internal salt such as shown for **9** is consistent with all the data presented. An attempt to methylate **9** with methyl iodide to prevent the formation of the internal salt was unsuccessful.

Attempts to hydrolyze the nitrile groups in **9** with 20% sulfuric acid or with sodium ethoxide were unsuccessful. With concentrated sulfuric acid **9** gave 4-quinolineacetamide (**11**) in one experiment and some 4-quinolylmalonamide (**10**) in another. The diamide **10** was easily converted into the monoamide **11** by further treatment with concentrated sulfuric acid. The ultraviolet spectrum of the monamide **11** was quite similar to that of the diamide **10**. In the infrared it showed one carbonyl band at 1670 cm^{-1}.

With alkaline 30% hydrogen peroxide the yellow compound **9** formed cinchoninic acid rather than the expected diamide **10**.

(4) W. Johnson, E. Worsch, and B. Buell, *J. Am. Chem. Soc.*, **71**, 1901 (1949).

(5) D. Mowry, *ibid.*, **67**, 1050 (1945).

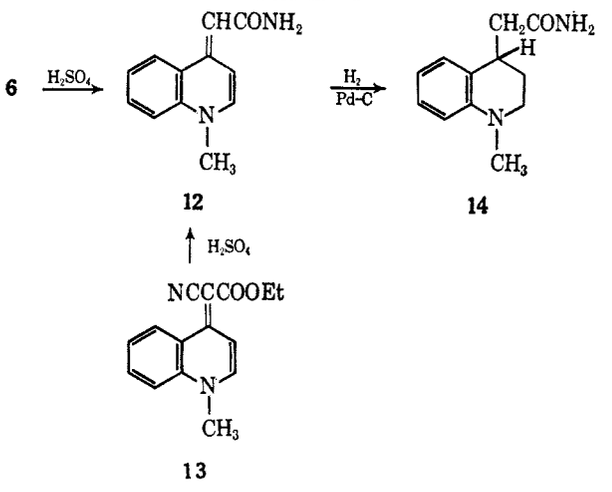
(6) Professor E. Campaigne (Department of Chemistry, Indiana University, Bloomington, Ind.), in reviewing our manuscript, expressed concern about the values of the extinction coefficients in the ultraviolet spectrum of **10** compared with **9**. It was felt that this substance might be the 1,2-dihydro derivative; however, the hydrolysis of **5** has been further investigated, and structure **10** is *confirmed* by additional data.

(7) W. S. Johnson and G. B. Buell, *J. Am. Chem. Soc.*, **74**, 4517 (1952).

(8) S. B. Knight, R. H. Wallick, and C. Balch, *ibid.*, **77**, 2577 (1955).

When 1-methyl-4-(α,α-dicyanomethylene)-1,4-dihydroquinoline (6) was treated with concentrated sulfuric acid followed by basification, a light yellow, relatively unstable compound (12) was isolated. Elemental analysis indicated $C_{12}H_{12}N_2O$ and its infrared spectrum was identical with that of the substance obtained by treating 1-methyl-4-(α-carbethoxy-α-cyanomethylene)-1,4-dihydroquinoline[9] (13) with sulfuric acid (Scheme II).

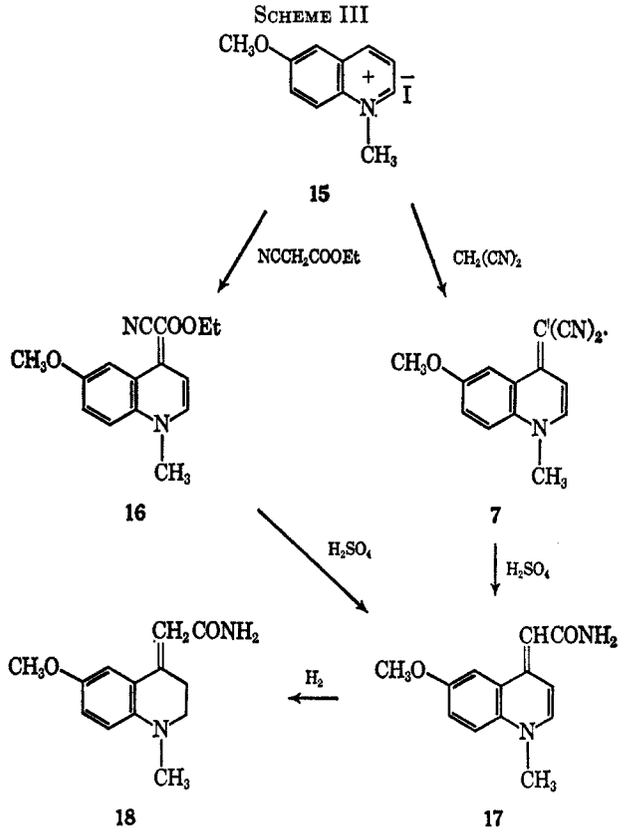
SCHEME II



Compound 6 was recovered unchanged after refluxing in dilute sodium hydroxide solution. Catalytic reduction of 12 produced a white crystalline compound 14 which analyzed for $C_{12}H_{14}N_2O$ indicating a tetrahydroquinoline nucleus. The nmr and infrared spectra were consistent with that expected for 1-methyl-1,2,3,4-tetrahydroquinoline-4-acetamide.

The condensation of 1-methyl-6-methoxyquinolinium iodide with malononitrile and with ethyl cyanoacetate, under conditions similar to those used with 1-methylquinolinium iodide[9] produced 1-methyl-4-(α,α-dicyanomethylene)-6-methoxy-1,4-dihydroquinoline (7) (Scheme III) and 1-methyl-4-(α-carbethoxy-α-cyanomethylene)-6-methoxy-1,4-dihydroquinoline (16), respectively. With concentrated sulfuric acid both 7 and 16 formed 1-methyl-4-(α-carbamylmethylene)-6-methoxy-1,4-dihydroquinoline (17). Reduction of 17 gave 1-methyl-6-methoxy-1,2,3,4-tetrahydroquinoline-4-acetamide (18).

SCHEME III



Experimental Section

All melting points were taken in capillary tubes and are uncorrected. The infrared spectra and ultraviolet spectra were recorded by a Beckman Model IR-5 and a Cary Model 14 spectrophotometer, respectively. The nmr spectra were determined with a Varian A-60.

4-(α,α-Dicyanomethylene)-1,2,3,4-tetrahydroquinoline (5).—To a mixture of 8 g of 4-keto-1,2,3,4-tetrahydroquinoline and 4 g of malononitrile in 100 ml of benzene was added a solution of 0.6 g of ammonium acetate in 25 ml of glacial acetic acid. This mixture was refluxed using a Dean–Stark trap until no more water separated. A total of approximately 1.2 ml was collected. When the orange benzene solution was evaporated in vacuum to a small volume, bright orange crystals separated and were collected by filtration and recrystallized from benzene, mp 155–156°, yield 6.5 g (62%).

Anal. Calcd for $C_{12}H_9N_3$: C, 73.83; H, 4.65; N, 21.52. Found: C, 74.01; H, 4.74; N, 21.64.

4-Quinolylmalonamide (10).—A solution of 0.9 g of 5 dissolved in 10 ml of concentrated sulfuric acid was heated on a steam bath for 1 hr. The hot solution was poured on crushed ice and made basic with 10% sodium hydroxide and then continuously extracted with benzene for 3 days. The benzene extract was evaporated to dryness and the white solid (yields varied from 40 to 80%) which separated was recrystallized from 95% ethanol, mp 212–214° dec. A sample crystallized from methanol benzene melted at 218–219°: λ_{max}^{MeOH} 286 mμ (ϵ 4700), 303 (4000), 318 (3400).

Anal. Calcd for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.33. Found: C, 62.75; H, 4.96; N, 18.27.

4-Quinolylmalononitrile Zwitterion (9).—A mixture of 1 g of 5 and 10 ml of 10% sodium hydroxide was refluxed for 6 hr. Copious evolution of ammonia was noted. The resulting yellow solution was cooled, filtered, and treated with 10% hydrochloric acid until the separation of the yellow solid was complete. The mixture was still basic. The yellow solid was isolated by filtration, washed with water, and dried, yield 0.36 g (36%). It was crystallized from 95% ethanol: mp 330°; ν_{max}^{KBr} (cm^{-1}) 3250 m, 3130 m, 3000 m, 2200 s, 2179 s, 1634 m, 1600 s, 1500 s, 1445 m, 1410 w, 1370 w, 1335 s, 1265 m, 1210 s, 1155 w, 1140 w, 850 w, 785 m, 750 m, 655 w; λ_{max}^{MeOH} 270 mμ (ϵ 7000), 280 (6500), 400 (20,000), 418 (25,000).

Anal. Calcd for $C_{12}H_7N_3$: C, 74.60; H, 3.65; N, 21.75. mol wt, 193. Found: C, 74.35; H, 3.74; N, 21.68. C, 74.14; H, 3.71; N, 21.64; mol wt, 193 (mass spectrometer), 195 (osmometer).

The filtrate was adjusted to pH 7 with 10% hydrochloric acid and extracted with ether. Evaporation of solvent gave 0.4 g (53% yield) of a yellow oil which was nearly pure as shown by thin layer chromatography (tlc) and whose infrared spectrum was identical with that of 4-keto-1,2,3,4-tetrahydroquinoline. Further extraction of the filtrate at pH 2 and 11 failed to give sufficient material to characterize.

4-Quinolineacetamide (11).—A solution of 0.2 g of 9 dissolved in 2 ml of concentrated sulfuric acid was heated on a steam bath for 1 hr and then poured on crushed ice. This mixture was made basic with 10% sodium hydroxide solution and then continuously extracted with benzene for 3 days. The benzene extract was evaporated to dryness leaving 0.07 g (40%) of white solid which was crystallized from acetone, mp 207–208°.

Anal. Calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04. Found: C, 70.66; H, 5.52; N, 15.13.

(9) N. Leonard and R. Foster, *J. Am. Chem. Soc.* **74**, 2110 (1952).

4-Quinolineacetamide is reported to have a melting point of 211–213°.[10]

In another experiment 0.2 g of **9** was dissolved in 2 ml of concentrated sulfuric acid and treated as described above. In this case the basic solution deposited 0.12 g (52%) of 4-quinolylmalonamide (**10**). Continuous extraction of the filtrate gave 0.05 g of 4-quinolineacetamide.

4-Quinolylmalonamide (0.1 g) dissolved in 1 ml of concentrated sulfuric acid was heated for 1 hr on the steam bath, poured on crushed ice, and extracted with benzene. There was obtained 45% (0.05 g) of quinolineacetamide.

Cinchoninic acid.—To a mixture comprising 0.2 g of **9**, 2 ml of 95% ethanol and 2 ml of 30% hydrogen peroxide cooled in an ice bath, was added 4 drops of 6 *N* sodium hydroxide. After the mixture was heated at 50° for 5 hr, the resulting solution was neutralized with 5% sulfuric acid and then evaporated to dryness under reduced pressure depositing 0.3 g of a white solid. Extraction of the white solid with absolute ethanol gave 0.14 g (82%) of cinchoninic acid, which was recrystallized from ethyl acetate, mp 244–245°. (The infrared spectrum was identical with that of authentic sample of cinchoninic acid.)

Anal. Calcd for $C_{10}H_7NO_2$: C, 69.36; H, 4.07; N, 8.09. Found: C, 69.34; H, 4.37; N, 8.10.

1-Methyl-4-(α-carbamylmethylene)-1,4-dihydroquinoline (12).—A solution of 4.0 g of **6** dissolved in 20 ml of concentrated sulfuric acid was heated on the steam bath for 1 hr. The hot solution was poured on crushed ice and then made basic with 20% sodium hydroxide solution. The resulting red solution was continuously extracted with benzene for 2 days. The benzene layer was separated and the yellowish-green precipitate, which separated from the aqueous layer, was isolated by filtration and dissolved in the benzene extract. Evaporation of the benzene solution to a small volume caused precipitation of yellowish needles, 2.6 g (65%) which were recrystallized from a benzene–acetone mixture: mp 150° dec (the crystals darken on standing); ν_{max}^{KBr} (cm^{-1}) 3380, 3150, 1625, 1590, 1540, 1500; $\lambda_{max}^{CH_3OH}$ 413 mμ (ε 16,000), 435 mμ (ε 14,400).

Anal. Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 71.81; H, 6.13; N, 13.78.

1-Methyl-4-(α-carbethoxy-α-cyanomethylene)-1,4-dihydroquinoline (**16**)[9] when similarly treated formed a product with an identical infrared spectrum.

1-Methyl-1,2,3,4-tetrahydro-4-quinoline Acetamide (14).—A solution of 2.6 g of **12** in 150 ml of absolute ethanol was reduced using 10% palladium on charcoal as the catalyst and 40 psi of hydrogen. The initially dark yellow solution turned colorless. The catalyst was removed by filtration and the clear filtrate was evaporated to dryness depositing 1.6 g (60%) of white crystals, which were recrystallized from benzene: mp 139–140°; nmr bands, τ 8.0 (quadruplet) (C_3 protons), 7.6 (complex doublet) (CH_2CONH_2), 7.1 s (NCH_3), τ 6.8 (complex triplet) (NH and C_4 proton); ν_{max}^{KBr} 3380 and 3150 (NH_2), 2800 (C_3 protons), 2940 (NCH_3), 1650 ($CONH_2$ carbonyl), 1630, 1600, and 1500 cm^{-1} (aromatic C=C).

Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90; N, 13.71. Found: C, 70.83; H, 7.64; N, 13.61.

1-Methyl-4-(α,α-dicyanomethylene)-6-methoxy-1,4-dihydroquinoline (7).—To a mixture of 15 g (0.05 mole) of 1-methyl-6-methoxyquinolinium iodide, 3.3 g (0.05 mole) of malononitrile, and 100 ml of absolute ethanol, cooled in an ice bath, was added a solution of 2.3 g (0.10 g-atom) of sodium in 50 ml of absolute ethanol with vigorous stirring. This mixture was stirred for 3 hr in an ice bath and then stirred at room temperature overnight. A yellow precipitate formed and was isolated by filtration, yield 4.7 g (40%). It was crystallized from nitromethane, mp 319–320°.

Anal. Calcd for $C_{14}H_{11}N_3O$: C, 70.87; H, 4.67; N, 17.71. Found: C, 70.74; H, 4.70; N, 17.71.

1-Methyl-4-(α-carboethoxy-α-cyanomethylene)-6-methoxy-1,4-dihydroquinoline (16).—To a mixture of 15 g (0.05 mole) of 1-methyl-6-methoxyquinolinium iodide, 5.65 g (0.05 mole) of ethyl cyanoacetate, and 100 ml of absolute ethanol, cooled in an ice bath, was added a solution of 1.2 g (0.05 g-atom) of sodium in 50 ml of absolute ethanol with vigorous stirring. The mixture was stirred at room temperature overnight. The yellow precipitate which formed was isolated by filtration and washed with acetone leaving 7.5 g of the starting quaternary salt. From the acetone solution 0.35 g (5%) of yellow needles were isolated and recrystallized from acetone, mp 219°.

Anal. Calcd for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.80; H, 5.72; N, 9.75.

1-Methyl-4-(α-carbamylmethylene)-6-methoxy-1,4-dihydroquinoline (17).—A solution of 2.0 g of **7** dissolved in 20 ml of concentrated sulfuric acid was heated for 1 hr on a steam bath. The hot solution was poured on crushed ice and then made basic with 20% sodium hydroxide. The resulting red solution was continuously extracted with benzene for 2 days. The benzene layer was separated and the yellowish precipitate, which separated from the aqueous layer, was isolated by filtration and dissolved in the benzene extract. Evaporation of the benzene solution to a small volume caused separation of yellow needles, 1.0 g (50%), which were recrystallized from a benzene–methanol mixture, mp 170° dec. The crystals darkened on standing.

Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.78; H, 6.20; N, 12.07.

The same substance (**17**) was obtained in 90% yield by treating a small quantity of 1-methyl-4-(α-carbethoxy-2-cyanomethylene)-6-methoxy-1,4-dihydroquinoline (**16**) with concentrated sulfuric acid for 1 hr at steam-bath temperature. The product was isolated as described above.

1-Methyl-6-methoxy-1,2,3,4-tetrahydro-4-quinolineacetamide (18).—A solution of 0.25 g of **17** in 150 ml of absolute ethanol was reduced using 200 mg of 10% palladium on charcoal and 40 psi of hydrogen until the initially colored solution turned colorless. The mixture was filtered to remove the catalyst and the clear filtrate was evaporated to dryness depositing 0.1 g (40%) of white crystals which were recrystallized from benzene, mp 101°.

Anal. Calcd for $C_{13}H_{18}N_2O_2$: C, 66.65; H, 7.75; N, 11.96. Found: C, 67.04; H, 7.96; N, 11.80.

Registry No.—**5**, 10147-02-1; **7**, 10182-03-3; **9**, 10147-03-2; **10**, 10147-04-3; **11**, 10147-05-4; **12**, 10182-04-4; **14**, 10147-06-5; **16**, 10147-07-6; **17**, 10147-08-7; **18**, 10147-09-8.

Acknowledgment.—The authors wish to thank Professor D. L. Coffen for his helpful discussion of spectral data.

(10) F. Zymalkowski and W. Schauer, *Arch. Chem.*, **290**, 218 (1957).

Synthesis of 1,3,7,9-Tetramethyl-2,4,6,8-tetraoxo-1,2,3,4,6,7,8,9-octahydropyrido[2,3-*d*:6,5-*d'*]-dipyrimidine from 6-Amino-1,3-dimethyluracil and Dimethyl Sulfoxide[1]

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Received September 29, 1966

Since dimethyl sulfoxide (DMSO) has become readily available considerable attention has been devoted to the diverse reactions which this compound displays. Under certain conditions it can serve as a source of formaldehyde. Nace and Monagle[2] noted the formation of formaldehyde during the reaction of DMSO with primary halides. Later Traynelis and Hergenrother[3] made a detailed study of products of the thermal decomposition of DMSO. On refluxing for 3 days it decomposes into methanethiol and formaldehyde as primary products. Other products isolated (dimethylthioformal, dimethyl disulfide, dimethyl sulfide, and dimethylsulfone) were accounted for as the result of

(1) This work was supported by Research Grant CA-02961 from the National Cancer Institute of the National Institutes of Health.

(2) H. R. Nace and J. R. Monagle, *J. Org. Chem.*, **24**, 1792 (1959).

(3) V. J. Traynelis and W. L. Hergenrother, *ibid.*, **29**, 221 (1964).