used. The monoacylated product, **3**, predominated. This indicates that $ZnCl_2$ is operating by a somewhat different mechanism than $AlCl_3$.

In general it seems that aluminum chloride is too active a complexing agent with 10-methylphenothiazine. While complexed with 10-methylphenothiazine, aluminum chloride probably prevents acylation; therefore acylation tends to take place on uncomplexed material. As the monoacylated product is less basic than 10-methylphenothiazine, it tends to be uncomplexed and is therefore preferentially acylated. This leads to multiple acylations and correspondingly poor yields of monoacylated product. Also, complexed **3** can acylate starting material to produce **5** and is removed by that path as well. In the case of 10-acylphenothiazine, the acyl group reduced the electron-donating properties of the phenothiazine and therefore reduces the strength of the complex with aluminum chloride. This can account for the better acylation yields for this compound reported in the literature.

Acylation apparently takes place on the surface of the insoluble zinc chloride. However, solvents such as chloroform can remove the acylated product and reduce secondary reactions. Another factor in favor of zinc chloride is that it is too weak a Lewis acid to complex irreversibly with the products. While this lowers reaction rates, they now tend to be related to the reactivity of the starting materials. Since the acid chloride and 10-methylphenothiazine are the most reactive materials present, formation of **3** is favored.

Experimental Section

10-Methylphenothiazine.—A method was used which is more convenient but similar in principle to those methods in the literature.[1,10] In this case, the strong base for removing the N proton from phenothiazine was made and used immediately in the same reaction vessel. Sodium (23 g, 1 g-atom) was added slowly in small pieces to 500 ml of dimethyl sulfoxide[11,12] under nitrogen with cooling to below 40° and stirring. After all of the metal had reacted, 100 g (0.5 mol) of phenothiazine was added slowly to maintain a temperature of 40°. Methyl iodide (142 g, 1 mol) was then added dropwise at 40°. The product was precipitated in water, filtered, and dried. The crude material, 107 g, was then chromatographed on a 1 × 30 in. silica gel column. The material eluted with benzene was recrystallized twice from ethanol–acetone (4:1), yield 91 g (86%), mp 97–100° (lit.[13] mp 99.5°).

Typical Procedure for Friedel–Crafts Reaction.—Chloroform was washed with water, and then dried over anhydrous calcium sulfate. Dry chloroform (700 ml), 85 g (0.4 mol) of 10-methylphenothiazine, and 60 g (0.4 mol) of β-carbomethoxypropionyl chloride[14] were mixed. Anhydrous zinc chloride (22 g, 0.16 mol) was added and the flask was heated to reflux at 63° with stirring for 4.5 hr. Formation of products was followed by thin layer chromatography in order to optimize the amount of monoacylated product. The reaction was quenched by cooling and addition of ice. After washing with water, the chloroform solution was evaporated. The products were dissolved in a minimum amount of benzene and chromatographed on a 1 × 28 in. silica gel column. Elution solvents were first benzene, then chloroform, then ethyl acetate. The eluted solvent was divided into 100-ml portions, which were evaporated separately. Separation of compounds was checked by tlc, and fractions containing two components were rechromatographed.

Unreacted 10-methylphenothiazine was eluted in the first 300 ml of benzene. There was a slight overlap with compound **5**. After rechromatographing, recovered 1 weighed 47 g (0.218 mol).

Methyl 4,4-Bis(10-methyl-3-phenothiazinyl)butene-3-oate (5) (Probable Assignment).—Compound **5** was eluted with benzene in the 300–1000-ml fractions. The fractions which overlapped with **1** were rechromatographed on silica gel with benzene. In drying, an amorphous, glassy solid, **5**, was obtained which had a single peak in tlc, weight 2.18 g (0.0042 mol).

Anal. Calcd for $C_{31}H_{26}N_2S_2O_2$: C, 71.4; H, 4.97; N, 5.36. Found: C, 71.36; H, 5.00; N, 5.56.

Methyl 4-(10-Methyl-3-phenothiazinyl)-4-oxobutanoate (3).—Elution of the column with 800 ml of 50:50 chloroform–benzene and 500 ml of $CHCl_3$ and solvent evaporation then produced **3**, crude yield 47 g (0.145 mol). **3** was first recrystalllzed from cyclohexane–benzene (2:1) and then from methanol–acetone (2:1), mp 113–116° (half width on a Du Pont 900 DTA at 20°/min).

Anal. Calcd for $C_{18}H_{17}SNO_3$: C, 66.1; H, 5.20; N, 4.28. Found: C, 66.07; H, 5.21; N, 4.41.

Dimethyl 4,4′-(10-Methyl-3,7-phenothiazinylene)di(4-oxobutanoate) (4).—Further elution of the column with 800 ml of chloroform eluted a yellow band of **4** in substantially pure form. It was recrystallized from 50:50 methanol–acetone, weight 2.36 g (0.0054 mol), mp 142–145°.

Anal. Calcd for $C_{23}H_{23}NO_6S$: C, 62.6; H, 5.21; N, 3.17. Found: C, 62.46; H, 5.22; N, 3.24.

Registry No.—**1**, 1207-72-3; **3**, 33214-29-8; **4**, 33214-30-1; **5**, 33214-31-2; $AlCl_3$, 7446-70-0; $ZnCl_2$, 7646-85-7.

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(10) H. Gilman, R. D. Nelson, and J. F. Champaigne, Jr., *J. Amer. Chem. Soc.*, **74**, 4205 (1952).
(11) A. Ledwith and N. McFarlane, *Proc. Chem. Soc.*, 108 (1964).
(12) D. E. O'Connor and W. I. Lyness, *J. Org. Chem.*, **30**, 1620 (1965).
(13) H. Gilman and R. D. Nelson, *J. Amer. Chem. Soc.*, **75**, 5422 (1953).
(14) G. M. Robinson and R. Robinson, *J. Chem. Soc.*, **127**, 180 (1925).

The Reaction of 4- and 5-Acetyloxazoles with Malononitrile

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Ring opening of oxazoles with nucleophilic reagents such as ammonia,[1-4] hydroxide,[5] and 2,4-dinitrophenylhydrazine[6] has been reported. We now wish to report the facile ring opening and subsequent recyclization of 4- and 5-acetyloxazoles with the nucleophile, malononitrile, in the presence of a base.

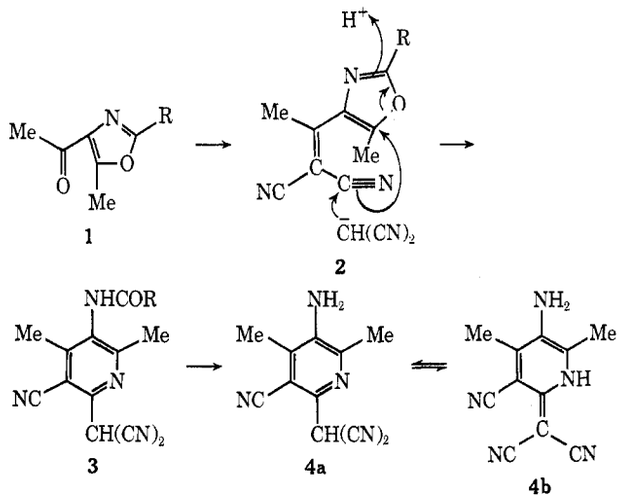
When 4-acetyl-2,5-dimethyloxazole[7] (**1**, R = CH_3) is allowed to react with 1 mol of malononitrile in the presence of potassium acetate, a small yield of the expected dicyanovinyl condensation product (**2**, R = CH_3) can be isolated. However, when 1 or 2 mol of malononitrile reacts with the acetyloxazole in the presence of sodium hydroxide, **2** is not obtained, but a different,

(1) S. Minovici, *Chem. Ber.*, **29**, 2097 (1896).
(2) G. Theilig, *ibid.*, **86**, 96 (1953).
(3) J. W. Cornforth and H. T. Huang, *J. Chem. Soc.*, 1960 (1948).
(4) A. Dornow and H. Hell, *Chem. Ber.*, **93**, 1998 (1960).
(5) J. W. Cornforth, *et al.*, *J. Chem. Soc.*, 1549 (1949).
(6) M. Ionescu and C. Makkay, *Stud. Univ. Babes-Bolyai, Ser. Chem.*, 121 (1966).
(7) A. Treibs and W. Sutter, *Chem. Ber.*, **84**, 96 (1951).

red, crystalline compound, $C_{11}H_9N_5$, precipitates. This red product also results by treating the dicyanovinyl derivative **2** (R = CH_3) with 1 mol of malononitrile.

On the basis of the spectroscopic and analytical evidence we assign structure **4** to the red compound and consider the mechanism shown in Scheme I as a

SCHEME I



possible route of formation. The infrared spectrum (KBr) showed the presence of at least two nitrile groups (peaks at ~2205 cm^{-1}). Several strong bands in the region 3160–3360 cm^{-1} suggested the presence of a primary amino group. Strong peaks were observed at 1640, 1590 (pyridine ring),[8] 1510, 1415, 1370 and 1385 (methyl groups), and 1270 and 1205 cm^{-1} (CN stretch[9]). The mass spectrum indicated the presence of a very stable molecular ion of *m/e* 211 and M^{2+} 105.5. Loss of $-CH_3$ (M − 15 = 196), HCN (M − 27 = 184), and $CH(CN)_2$ (M − 65 = 146) were prominent features. The loss of the $CH(CN)_2$ fragment in the mass spectrum of **2** was an extremely unfavorable process. The nmr spectrum (in pyridine-d_5) indicated the presence of two methyl groups at δ 2.14 and 2.85.

Under the conditions employed (aqueous ethanol and NaOH at 100°) it is likely that the second molecule of malononitrile had attacked the carbon of the nitrile in **2** yielding **3**. This type of addition is well known with malononitrile and has been shown to occur in the condensation with *o*-hydroxyacetophenone,[10] with 2,4-diketones,[11,12] and with the enamines[13] under basic conditions.

The conversion of **2** to **3** is probably best envisaged as attack by the second molecule of malononitrile on one of the nitrile groups, followed by concerted opening of the oxazole ring. This step would be favored by resonance stabilization of the pyridine ring so formed. When the carbonyl group is blocked, *e.g.*, by toluenesulfonylhydrazide, the reaction does not proceed at all, suggesting that formation of the dicyano vinyl derivative **2** is a necessary initial step before opening of the oxazole ring can occur.

Compound **4** is expected to be tautomeric[10,12,13] (**4a** ⇌ **4b**). While we have not attempted to measure the position of this tautomeric equilibrium, the strong fluorescence and intense color of the product indicates[12,14,15] that **4b** is a significant contributor. Reversible protonation results in an intense blue color and quenching of the fluorescence.

The reaction between 1 mol of malononitrile and either 5-acetyl-4-methyloxazole[4] (**5**, R = H) or 5-acetyl-2,4-dimethyloxazole[4] (**5**, R = CH_3) in the presence of catalytic amounts of KAc gave the expected dicyanovinyl condensation product **6** in low yield. With 1 or 2 mol of malononitrile in the presence of aqueous sodium hydroxide **6** was not isolated but the same yellow crystalline compound was obtained with either **5** (R = H) or **5** (R = CH_3). The liberation of ammonia was also observed during this reaction.

Elemental analysis and the mass spectrum (*m/e* 212) of the yellow material coresponded to $C_{11}H_8N_4O$. The infrared spectrum (KBr) indicated the presence of a primary amino group (ν_{NH} = 3150 and 3300 cm^{-1}). Strong bands at 2218 and 2225 cm^{-1} indicated the presence of at least two nitrile groups, while the presence of *C*-methyl groups was suggested by absorptions at 1375 and 1388 cm^{-1}. Medium-to-strong absorptions were observed at 1660, 1585, 1595, 1540, 1325, and 1030 cm^{-1}. A strong band at 1680 cm^{-1} suggested the presence of carbonyl group conjugated with amino function (*i.e.*, an amide carbonyl).

Confirmation of the presence of a primary amino group was provided by Purdie methylation (CH_3I–Ag_2O) of the yellow compound. The product, mp 194–195°, analysis and mass spectrum (*m/e* 240) corresponding to $C_{13}H_{12}N_4O$, lacked the prominent ir absorptions in the region 3150–3300 cm^{-1}, but a strong peak at 1412 cm^{-1} indicated the presence of an $N(CH_3)_2$ group.

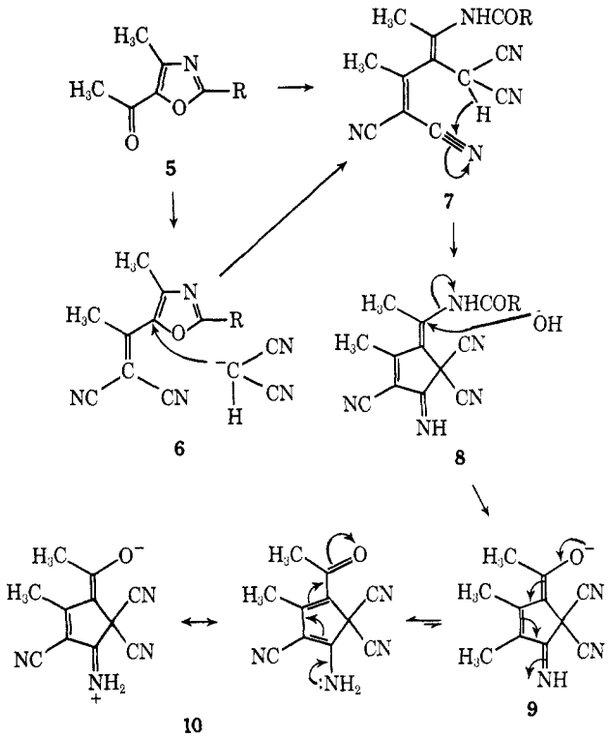
It is worthy of note that in the dimethylated compound the closely spaced bands at 1585 and 1595 cm^{-1} and also the band at 1470 cm^{-1} are absent, while the two spectra are otherwise remarkably similar.

The nmr spectrum of the yellow compound showed (in DMSO-d_6) a broad signal at δ 9.10, which disappeared on deuterium exchange with DCl–D_2O, and also was absent in the spectrum of the dimethylamino derivative. Two methyl resonances were prominent at δ 2.19 and 2.15 in both the yellow compound and in its dimethyl derivative. In the latter the $N(CH_3)_2$ resonance was observed as a singlet (with the correct integral) at δ 3.04. Consideration of the available spectroscopic and chemical data leads us to suggest structure **10** for the yellow product.

The formation of **7** (see Scheme II) by nucleophilic attack of $CH(CN)_2$ on C_5 of either **5** or **6** is considered likely because it is flanked by two strongly electron-withdrawing groups. Ring closure **7** → **8** is possibly favored by the relative proximity of the vinyl nitrile and dicyanomethide anion obtained by proton loss from the dicyanomethyl group under the alkaline conditions employed.

(8) A. R. Katritzky, *Quart. Rev. Chem. Soc.*, **13**, 353 (1959).
(9) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964.
(10) H. Junek, *Monatsh. Chem.*, **95**, 234 (1964).
(11) R. Hull, *J. Chem. Soc.*, 1136 (1951).
(12) H. Junek, *Monatsh. Chem.*, **95**, 1201 (1964).
(13) H. Junek, *ibid.*, **95**, 1473 (1964).
(14) P. Bosshard and C. H. Eugster, *Advan. Heterocycl. Chem.*, **7**, 378 (1966).
(15) A. T. Balaban, G. D. Mateescu, and M. Elian, *Tetrahedron*, **18**, 1083 (1962).

SCHEME II



Nucleophilic displacement of NHCOR by $^-$OH is in agreement with the finding that the yellow compound can be derived from either **5** (R = H) or **5** (R = Me).

Experimental Section

Microanalyses were performed by the Australian Microanalytical Service, CSIRO, Melbourne. The nmr spectra were recorded on a Varian Associates A-60D instrument; ir spectra were recorded on a Perkin-Elmer 225 spectrometer. Mass spectra were recorded by courtesy of Dr. G. Wunderlich, CSIRO Division of Organic Chemistry, Melbourne.

4-Acetyl-2,5-dimethyloxazole (**1**, **R** = **CH$_3$**) was prepared according to the procedure of Treibs and Sutter,[7] mp 49.0–49.5° (lit.[7] mp 49°).

2,5-Dimethyl-4-(β,β-dicyano-α-methylvinyl)oxazole (**2**, **R** = **CH$_3$**).—4-Acetyl-2,5-dimethyloxazole (0.35 g, 0.0025 mol), malononitrile (0.165 g, 0.0025 mol), and dry potassium acetate (0.01 g) were refluxed in dry benzene (20 ml) for 44 hr. Removal of the solvent *in vacuo* afforded a brown oil which was chromatographed on an aluminum oxide (BDH) column using benzene–petroleum spirit (bp 60–80) (1:1) as elutent. Unreacted 4-acetyl-2,5-dimethyloxazole (0.15 g) and **2** (R = CH$_3$) (0.1 g), mp 130–131°, were obtained as colorless needles: ir 2240 (CN), 1621 cm^{-1} (C=N); mass spectrum M$^+$ 187, 187 → 91 [loss of (CN)$_2$C=C(CH$_3$)$_2$].

Anal. Calcd for $C_{10}H_9N_3O$: C, 64.17; H, 4.81; N, 22.46. Found: C, 64.30; H, 4.80; N, 22.34.

3-Amino-5-cyano-6-(dicyanomethyl)-2,4-dimethylpyridine (**4**).—To 4-acetyl-2,5-dimethyloxazole (0.7 g, 0.005 mol) in ethanol (10 ml) and aqueous sodium hydroxide (3 ml, 2 *N*) was added malononitrile (0.66 g, 0.01 mol) in water (10 ml). The resulting red solution was heated on a steam bath for 20 min, cooled in ice, filtered, and washed with water. 3-Amino-5-cyano-6-(dicyanomethyl)-2,4-dimethylpyridine (**4**) (0.32 g, 33%) crystallized from aqueous DMF (1:1) as red needles, mp >300° dec.

Anal. Calcd for $C_{11}H_9N_5$: C, 62.56; H, 4.26; N, 33.17. Found: C, 62.34; H, 4.25; N, 33.65.

Reaction of 2,5-Dimethyl-4-(β,β-dicyano-α-methylvinyl)oxazole with Malononitrile.—2,5-Dimethyl-4-(β,β-dicyano-α-methylvinyl)oxazole (0.09 g, 0.0001 mol) in ethanol (5 ml) and aqueous sodium hydroxide (1 ml, 2 *N*) were treated at 25° with malononitrile (0.007 g, 0.0001 mol) in water (1 ml). After heating the red solution on a steam bath for 20 min, the solvent was removed, water (2 ml) was added, and the precipitate was collected, washed with water, and recrystallized from aqueous DMF (1:5) to yield material (0.01 g) identical (mass spectrum, ir) with **4**.

5-Acetyl-4-methyloxazole (**5**, **R** = **H**).—This was prepared according to the method of Dornow and Hell,[4] bp 68–74° (10–12 mm) [lit.[4] bp 74–75° (15 mm)].

5-Acetyl-2,4-dimethyloxazole (**5**, **R** = **CH$_3$**) was prepared according to the procedure of Dornow and Hell[4] as colorless needles from petroleum spirit (bp 60–80°), mp 58–59° (lit.[4] mp 61°).

Anal. Calcd for $C_7H_9NO_2$: C, 60.48; H, 6.53; N, 10.08. Found: C, 60.52; H, 6.61; N, 10.31.

2,4-Dimethyl-5-(β,β-dicyano-α-methylvinyl)oxazole (**6**, **R** = **CH$_3$**).—5-Acetyl-2,4-dimethyloxazole[4] (1.39 g, 0.01 mol), malononitrile (0.66 g, 0.01 mol), dry potassium acetate (0.01 g), and dry benzene (25 ml) were refluxed for 26 hr with water removal (Dean and Stark apparatus). Removal of the solvent *in vacuo* followed by addition of water (20 ml) to the residue and extraction with ethyl acetate gave after drying ($MgSO_4$) and evaporation of the solvent a brown oil. This was dissolved in benzene (10 ml) and petroleum spirit (bp 40–60°) was added dropwise to turbidity. After 5 days at 0° the crystals that deposited were collected, washed with petroleum spirit (bp 40–60°), and recrystallized twice (charcoal) from water to afford **6** (R = CH$_3$) (0.2 g) as colorless needles: mp 88–89°; ir 2200 cm^{-1} (CN); nmr δ 2.55 (s, 6, 2 CH$_3$), 2.46 (s, 3, CH$_3$).

Anal. Calcd for $C_{10}H_9N_3O$: C, 64.22; H, 4.85; N, 22.47. Found: C, 64.28; H, 4.80; N, 22.29.

2-Acetyl-5-amino-4-cyano-1,1-dicyano-3-methylcyclopentadiene (**10**).—5-Acetyl-4-methyl- or 5-acetyl-2,4-dimethyloxazole (**5**) (0.01 mol) in ethanol (25 ml) and aqueous sodium hydroxide (5 ml, 2 *N*) was treated at 20° with malononitrile (0.02 mol) in water (5 ml). The red solution was heated on a steam bath for 15 min (NH$_3$ evolved), cooled to 20°, and neutralized with hydrochloric acid (12 *N*), water (100 ml) was added, and the yellow precipitate was collected and washed with water and then aqueous alcohol (1:1). **10** (60%) crystallized from aqueous DMF (1:3) as yellow needles, mp = 300° dec.

Anal. Calcd for $C_{11}H_8N_4O$: C, 62.26; H, 3.77; N, 26.41. Found: C, 62.48; H, 4.04; N, 26.17.

2-Acetyl-4-cyano-1,1-dicyano-5-dimethylamino-3-methylcyclopentadiene.—The yellow compound **10** (0.1 g), silver oxide (0.1 g), and methyl iodide (30 ml) were vigorously shaken in a stoppered flask at 20° for 16 hr. The red solution was filtered, the volume of the filtrate reduced *in vacuo* by two-thirds, and the red precipitate collected and washed with aqueous alcohol (2:1). The dimethylamino derivative of **10** crystallized from aqueous acetone (1:8) as red needles (0.1 g, 88%), mp 194–195°.

Anal. Calcd for $C_{13}H_{12}N_4O$: C, 65.05, H, 5.04; N, 23.35. Found: C, 65.18; H, 5.29; N, 23.21.

Registry No.—**1**, 23000-12-6; **2** (R = Me), 33303-94-5; **4**, 33223-92-6; **5** (R = H), 23012-19-3; **5** (R = Me), 23012-25-1; **6** (R = Me), 33223-95-9; **10**, 33223-96-0; **10** dimethylamino derivative, 33223-97-1; malononitrile, 109-77-3.

Reactions of Triphenylarsonium and Triphenylphosphonium Phenacylides with 1-*p*-Nitrobenzoylaziridine

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The chemistry of triphenylarsonium phenacylide (**1**) has recently been investigated and compared with that of triphenylphosphonium phenacylide (**2**).[1] It was observed that **1** and **2** showed the same sensitivity to hydrolysis and oxidation, and both gave O-alkylated

(1) A. W. Johnson and H. Schubert, *J. Org. Chem.*, **35**, 2678 (1970).