Iminopropadienones from Dioxanediones, Isoxazolopyrimidinones, Pyridopyrimidinones, and Pyridopyrimidinium Olates

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Iminopropadienones, RN=C=C=C=O, can be generated from four different types of precursors in flash vacuum thermolysis reactions: 1,3-dioxane-4,6-diones, isoxazolopyrimidinones, pyridopyrimidinium olates, and pyridopyrimidinones. 2,6-Difluorophenyl-, 2,6-diethylphenyl-, o-tert-butylphenyl-, and mesityliminopropadienone have been directly observed by Ar matrix IR spectroscopy in one or more of these reactions. Reactions with bis-nucleophiles afford pyridopyrimidinones and perhydrodiazepinone derivatives.

Introduction

We have reported the formation of iminopropadienones, RN=C=C=C=O, by flash vacuum thermolysis (FVT) of 1,3-dioxane-4,6-dione (Meldrum’s acid) derivatives and, in a preliminary communication, isoxazolopyrimidinones. Pyridopyrimidinium olates of type are obtained by addition of iminopropadienones to 2-(methylamino)pyridine, and in the case of the mesityl derivative, it was shown that compound was again cleaved to mesityliminopropadienone and 2-(methylamino)pyridine on FVT. We have now found that both mesoionic pyridopyrimidinium olates and pyrimidopyrimidinones of type can be used as precursors of a variety of aryliminopropadienones.

Results and Discussion

2,6-Difluorophenyliminopropadienone was generated from three different types of precursor, the Meldrum’s acid derivatives and, the isoxazolopyrimidinone, and the mixture of isomeric pyridopyrimidinium olates and pyrimidopyrimidinones (Scheme 1). The Meldrum’s acid precursor was synthesized by reaction of 5-(bismethylthiomethyl)-2,2-dimethyl-1,3-dioxane-4,6-dione with 2,6-difluorobenzaldehyde by adaptation of a standard procedure. A 1:1 mixture of olates and pyrimidopyrimidinones of type was obtained by condensing the FVT product on a coldfinger at 77 K. After the end of the thermolysis, a solution of a trapping agent is injected onto the coldfinger, and the product is isolated after warming to room temperature. The two regioisomers and were not separable by chromatography, but the “normal” isomer crystallized selectively.
from CHCl₃ and was characterized by X-ray crystallography. On FVT of the mixture of 7a and 7b at 550 °C, both isomers were fully converted to 8 (Scheme 1 and Figure 1).

Figure 1 shows the Ar matrix IR spectra obtained from the three precursors compared with the calculated spectrum at the B3LYP/6-31G** level of theory. It is clearly seen that the same compound is obtained in all cases, whereby the isoxazolopyrimidine (6) route is particularly useful because the few byproducts (HCN and HNCO) do not disturb the spectrum, and furthermore they are rather nonnucleophilic, so they do not impede the subsequent preparative reactions of the iminopropadienone. The mechanism of formation of RNCCCO from 6 is believed to involve breakage of the N–O bond to generate a putative vinylnitrene, which, when R = aryl, undergoes a 1,2-shift of R from C to N. The resulting ketenimine undergoes a cycloreversion to HCN, HNCO, and RNC−CCO. The chemistry of 8 is unusual in several respects. The normal mode of reaction of iminopropadienones with bis-nucleophiles is a rapid reaction with the strongest nucleophile at the highly electrophilic C=O group, followed by a slower reaction at the less electrophilic C=N group. With mononucleophiles, this leads to malonic acid imide derivatives (e.g. 9, Scheme 1, and 15, Scheme 2), and with bis-nucleophiles, heterocyclic compounds are generated. In some cases minor amounts of the products of the opposite mode of addition are formed, corresponding to initial addition of the weaker nucleophile to the C=O group or initial addition of the stronger nucleophile to the C=N group, but the “normal” mode always dominates. The formation of a 1:1 mixture of 7a and 7b is highly unusual and indicates that the electron-withdrawing effect of fluorine may have increased the electrophilicity of the C=N group in 8. A similar phenomenon is observed in the reaction with the unsymmetrical N-methylethylenediamine to afford two perhydridazepinones, 10a and 10b, in a 1:1 ratio (Scheme 1). Naturally, the reaction with the symmetrical N,N'-dimethylethylenediamine afforded a single diazepinone, 11.

The chemistry of the difluoro compound 8 is contrasted with that of the diethyl analogue 13 in Scheme 2. 13 Was obtained by FVT of the Meldrum's acid derivatives 12 and 12', themselves synthesized by reaction of 2,6-diethylphenyl isothiocyanate with Meldrum's acid, followed by S-methylation with methyl iodide and nucleophilic replacement of the methylthio group with dimethylamine. The iminopropadienone 13 was identified by its Ar matrix IR spectrum (Figure S1). Like 8, 13 is not isolable at room temperature, and the preparative chemistry was performed as outlined above. Reaction with diethylamine gave the malonic imide derivative 15. With 2-(methylamino)pyridine, only one product, 14, corresponding to the “normal” mode of addition, was obtained. Also with N-methylethylenediamine, only one product, 16, was obtained, corresponding to addition of the more nucleophilic NMe group to the C=O function. N,N'-dimethylethylenediamine afforded the diazepinone derivative 17. Thus, the diethyl derivative 13 exhibits the


normal reactivity pattern similar to the neopentyl, the o-tert-butylphenyl (19a), and the mesityl (19b) derivatives.2

Compound 19a was prepared by FVT of the Meldrum’s acid derivative 18a as previously described.2 Reaction with 2-aminopyridine and 2-(methylamino)pyridine afforded the pyridopyrimidinone 20a and the olate 21a, respectively (Scheme 3). FVT of both 20a and 21a regenerated the iminopropadienone 19a (Figure 2).

In the case of the mesityl derivative 19b, obtained from the Meldrum’s acid derivative 18b, it has already been shown that the olate 21b regenerates the iminopropadienone.2 This also happens on FVT of the pyridopyrimidinone 20b (Scheme 3 and Figure S2). Unlike the difluorophenyl case described above, the isoxazolopyrimidinone 22b is not a good iminopropadienone precursor: while 19b can be identified by its strong absorption

**FIGURE 1.** IR spectra of 2,6-difluorophenyliminopropadienone 8 (a) generated by FVT of dioxanedione 5 (Ar matrix, 8 K), (b) by FVT of the 1:1 mixture of pyridopyrimidinium olates 7a and 7b (Ar matrix, 8 K), (c) by FVT of isoxazolopyrimidinone 6 (Ar matrix, 8 K), (d) DFT-calculated spectrum (B3LYP/6-31G**: scaling factor 0.9613). 2,6-Difluorophenyliminopropadienone 8: 2247, 2145, 2137, 1636, 1483, 1017 cm\(^{-1}\). (A) acetone: 1720, 1364, 1217, 1092 cm\(^{-1}\). (C) carbon dioxide: 2345, 2340, 663 cm\(^{-1}\). (D) dimethylamine: 2975, 2832, 1148 cm\(^{-1}\). (M) 2-(methylamino)pyridine: 1612, 1602, 1578, 1524, 1511, 1421, 771 cm\(^{-1}\). (H) HNCO: 2259 cm\(^{-1}\) (also present but not shown 3518, 3507, 770 cm\(^{-1}\)).
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at 2240 cm\(^{-1}\), the yield was low, and unidentified byproducts were formed.\(^5\)

The 2,4- and 2,5-dimethoxyiminopropadienones 23 and 24 have also been prepared by FVT of the corresponding Meldrum’s acid derivatives. The preparative procedures and matrix IR spectra are presented in the Supporting Information (Figures S3 and S4).

Mechanism of Cleavage of Pyridoprimidinones.

What is the mechanism of formation of iminopropadienones from the neutral and mesoionic pyridoprimidinones? It is known that 2-substituted pyridoprimidinones of type 25 (X = Cl, MeS, or NMe\(_2\)) undergo elimination of HX under FVT conditions to generate 2-pyridyliminopropadienone 29.\(^6,6\) The reaction is believed to take place via the intermediates 26 and 27, as indicated in Scheme 4. Why is this pathway not followed for the corresponding hydroxy derivatives (i.e., 25) in the case of the pyridopyrimidinones? An explanation is given in Scheme 4. In 2-aminopyridopyrimidinones 25, where X = NHR, tautomerization can populate the mesoionic form 30. This type of tautomerization is known for the corresponding hydroxy derivatives (i.e., 25, X = OH).\(^7\) It is also known that the non-mesoionic pyridoprimidinones have somewhat lower energies than the mesoionic ones, but the difference is not large.\(^4\) Ring opening\(^6,6\) of mesionic 30 will lead to the transient ketene 31, which can undergo a cycloelimination to 1H-2-iminopyridine 33 and the iminopropadienones 32 (19). Compound 33 tautomerizes to 2-aminopyridine.\(^9\)

However, when X = NHR or OH, tautomerization of 25 cannot take place, and the normal ring opening yields 26 and hence 27 and 28, and 1,4-cleavage leads to the observed product, 2-pyridyliminopropadienone 29. We find that the mesoionic 1-methylpyridoprimidinones usually undergo cleavage to RNCCCO at FVT temperatures of ca. 350–550 °C. The nonmesoionic 2-aminopyridopyrimidinones require much higher temperatures, on the order of 800 °C. Thus, provided the initial barrier to tautomerization (25 → 30) can be overcome, the mesoionic pathway will dominate.

Thus, by proper choice of leaving group—secondary or tertiary amine—it is possible to synthesize a range of (substituted) phenyl- and pyridoprimidinopropadienones, and the pyridoprimidinones 25 emerge as a very versatile group of precursors. This is particularly important, because it is not possible to obtain 2-pyridyliminopropadienones from acid’s acid precursors.\(^5,10\)

Figure 2. IR spectra of 2-tert-butyphenyliminopropadienone 19a (a) generated by FVT of dioxanenone 18a (Ar matrix, 8 K), (b) by FVT of pyridoprimidinone 20a (Ar matrix, 8 K), (c) by FVT of pyridoprimidinium olate 21a (Ar matrix, 8 K), and (d) DFT-calculated spectrum (B3LYP/6-31G**; scaling factor 0.9613). 2-tert-Butylphenyliminopropadienone 19a: 2790, 2237, 2138, 1624, 1354, 730, 530 cm\(^{-1}\). (A) acetone: 1720, 1364, 1279, 1092 cm\(^{-1}\). (D) dimethylamine: 2975, 2832, 1148, 1021 cm\(^{-1}\). (C) carbon dioxide: 2341, 663 cm\(^{-1}\). (M) 2-(methylamino)pyridine: 1612, 1578, 1524, 1484, 1445, 1317, 1273, 1149, 735 cm\(^{-1}\).

Conclusion

Meldrum’s acid derivatives, isoxazolopyrimidinones, pyridoprimidinones, and pyridoprimidinium olate can all be used as precursors of iminopropadienones, RNCCO. There are two mechanisms of fragmentation of pyridoprimidinones 25, which, by using either tertiary or secondary amine substituents, can be harnessed at will to produce either 2-pyridyliminopropadienones or aryliminopropadienones. 2,6-Difluorophenyliminopropadienone shows unusual reactivity, being indiscriminate in its reactions with nucleophiles at the C=O vs C=N bonds. The origin of this effect is the subject of an ongoing investigation.
Experimental Section

The FVT apparatus and general equipment were as previously reported.

Meldrum's Acid Route. 5-(2,6-Difluorophenilamino)methylene-2,2-dimethyl-1,3-dioxane-4,6-dione 5. A solution of 12.4 g (50 mmol) of 5-[(bis(methylthio)methylene)ylthio)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione 5. was then either heated at 50 °C for 24 h in a closed round-bottom flask or heated in a minireactor at 90 °C under high pressure (1000 psi) for 6 h. (CAUTION: The heating in a closed system or under pressure should be carried out in an apparatus equipped with a proper safety valve.) The resulting solution was concentrated under reduced pressure, then 5 mL of hexane was added to precipitate white crystals, which were collected by filtration and recrystallized from hot THF to give 6.9 g (yield 70%) in colorless crystals: mp 145 °C; 1H NMR (400 MHz, CDCl₃) δ = 1.67 (s, 6 H), 2.89 (s, 6 H), 6.96 (t, J = 8.4 Hz, 2H), 7.17–7.22 (m, 1H), 9.23 (s, br, 1H, NH); 13C NMR (100 Hz, CDCl₃) δ = 26.2, 41.4, 76.2, 102.3, 112.1, 116.7, 127.7, 157.3 (dd, JCF = 252 Hz), 164.3, 165.2. Anal. Calcd for C₁₈H₂₃NO₄S: C, 50.93; H, 4.04; N, 3.96. Found: C, 50.93; H, 4.04; N, 4.04.

2,6-Diethylphenyl isothiocyanate was prepared by the procedure of Habib et al., with modifications. 2,6-Diethylaniline (15.0 g, 100 mmol) and phenyl isothiocyanate (29.7 g, 220 mmol) were heated under reflux for 24 h, whereupon a white flaky crystalline sublimate of diphenylthiourea appeared in the condenser. The mixture was cooled, quenched with 100 mL of petroleum spirit (bp 60–90 °C), filtered, and the filtrate was evaporated to dryness. The product was purified by vacuum distillation (1 × 10⁻⁴ mbar) to afford 17.2 g of colorless oil (90%): bp 178 °C; IR (KBr) ν 3064, 2087, 1801, 1593 cm⁻¹. 1H NMR (200 MHz, CDCl₃) δ 1.44 (t, J = 7.5 Hz, 6H), 2.90 (q, J = 7.5 Hz, 4H), 7.22–7.38 (m, 3H); 13C NMR (50 Hz, CDCl₃) δ 14.2, 25.6, 126.4, 127.3, 128.1, 134.9, 140.8.

5-(2,6-Diethylanilino)(methylthio)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione 5. A solution of 14.4 g (100 mmol) of isopropylidene malonate (Meldrum's acid) and 28 mL of triethylamine (200 mmol) in 70 mL of dry acetonitrile was stirred for 30 min, then 19.1 g (100 mmol) of 2,6-diethylphenyl isothiocyanate was added, and the mixture was heated at 60 °C for 12 h. A total of 7.0 mL (100 mmol) of idomethane was added dropwise to the mixture at room temperature and the resulting solution was then stirred for 48 h. The resulting solution was concentrated under reduced pressure, then 5 mL of x-hexane was added to precipitate yellow crystals, which were collected by filtration and recrystallized from hot THF to give 21.0 g (yield 60%) as pale yellow crystals: mp 150–151 °C; 1H NMR (400 MHz, CDCl₃) δ 1.19 (t, J = 7.5 Hz, 6H, CH₃), 1.73 (s, 6 H, CMe₂), 2.35 (s, 3 H, SCH₃), 2.49–2.62 (m, 4H, CH₂), 2.75 (t, J = 7.6 Hz, 2H), 5.53 (t, J = 7.6 Hz, 1H), 7.12 (s, br, 1H, NH). 13C NMR (50 Hz, CDCl₃) δ 26.2, 41.4, 76.2, 102.3, 112.1, 116.7, 127.7, 157.3 (dd, JCF = 252 Hz), 164.3, 164.6, 164.8. Anal. Calcd for C₁₉H₂₆N₂O₄: C, 55.21; H, 9.72; N, 14.0. Found: C, 55.11; H, 9.62; N, 14.0.

5-(2,6-Diethylanilino)(dimethylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione 12 was prepared from 12 (12.2 g, 35 mmol) as described for 5 above to give 8.5 g (yield 70%) by the first method and 10.9 g (yield 90%) by the second method as colorless crystals: mp 199–200 °C; 1H NMR (400 MHz, CDCl₃) δ 1.18 (t, J = 7.7 Hz, 6H, CH₃), 1.73 (s, 6 H, 2.40–2.63 (m, 4H), 2.66 (s, 6 H), 7.12 (d, J = 7.6 Hz, 2H), 2.72 (t, J = 7.4 Hz, 2H), 7.45 (d, J = 7.5 Hz, 2H), 9.65 (s, br, 1H, NH). 13C NMR (100 Hz, CDCl₃) δ 14.0, 24.3, 26.1, 41.2, 75.3, 102.0, 126.7, 129.3, 134.0, 140.8, 163.9(CO), 180.1(C–C) (the assignment of the peaks was supported by 2DQC and HMBC experiments). Anal. Calcd for C₁₉H₂₆NO₅: C, 66.97; H, 6.62; N, 3.96. Found: C, 66.78; H, 6.69; N, 3.96.

FVT with Argon Matrix Isolation. 2,6-Difluorophenylisopropionamide 8. 5-(2,6-Diethylanilino)(dimethylamino)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione 5 (10 mg, 0.03 mmol) was sublimed at 70 °C through the FVT apparatus equipped with a proper safety valve. The resulting solution was concentrated under reduced pressure, then 5 mL of hexane was added to precipitate white crystals, which were collected by filtration and recrystallized from hot THF to give 21.0 g (yield 60%) as pale yellow crystals: mp 150–151 °C; 1H NMR (400 MHz, CDCl₃) δ 1.19 (t, J = 7.5 Hz, 6H, CH₃), 1.73 (s, 6 H, CMe₂), 2.35 (s, 3 H, SCH₃), 2.49–2.62 (m, 4H, CH₂), 2.75 (t, J = 7.6 Hz, 2H), 5.53 (t, J = 7.6 Hz, 1H), 7.12 (s, br, 1H, NH). 13C NMR (50 Hz, CDCl₃) δ 26.2, 41.4, 76.2, 102.3, 112.1, 116.7, 127.7, 157.3 (dd, JCF = 252 Hz), 164.3, 164.6, 164.8. Anal. Calcd for C₁₉H₂₆NO₅: C, 65.87; H, 7.56; N, 3.96. Found: C, 65.71; H, 7.78; N, 7.94.
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1148 w, 1021 w cm⁻¹ (dimethylamine); 2346, 2340, 664 m cm⁻¹ (carbon dioxide).

2,6-Diethylnitromethyleniminoprodienone 13. 5-(2,6-Diethylphenylimino)methyl)-1,2-dimethyl-1,3-dioxane-4,6-dione 12 (10 mg, 0.03 mmol) was sublimed at 70 °C through the FVT tube at 700 °C (the system was operated at a pressure of 2 mbar and thermolyzed at 700 °C over the course of 3 h; also present were the following peaks: 1710 m, 1365 m, 1227 m (carbon dioxide). 1H NMR (400 MHz, CDCl₃) δ 3.51 (m, 4H), 6.83 (t, 3H), 2.64 (q, 3H), 3.47 (s, 2H), 3.48 (s, 2H), 3.49 (s, 2H), 3.51 (s, 2H), 3.53 (m, 3H), 6.32 (s, 2H), 6.38 (t, 3H); 13C NMR (50 Hz, CDCl₃) δ 35.8, 37.1, 38.0, 49.4, 50.4, 111.3 (m), 122.0 (t), 127.2 (t), 127.2 (t), 152.2 (dd, J = 141 Hz, 155.2 (dd, J = 142 Hz), 156.3, 164.9. Anal. Calcd for C₁₉H₂₁N₃O: C, 74.24; H, 6.89; N, 13.67.

1-Methyl-7-(2,6-diethylnitromethyleniminofuran-4,6-diones

1,4-Dimethyl-7-(2,6-difluorophenylimino)perhydro[1,4]diazepin-5-one 11. To iminoprodienone 8, obtained from Meldrum’s acid derivative 5 (329 mg, 1.0 mmol), was injected a solution of 97.0 mg (1.1 mmol) of N,N-dimethylamidine in 30 mL of dry THF, and the resulting mixture was stirred for 3 days. The solvent was evaporated, and the crude product was purified by flash chromatography (silica gel, 5% MeOH/ether) to yield 75 mg (30%) of 10a/10b in a 1:1 ratio as a yellow oil: IR (KBr) ν 3255, 1661, 1645, 1617 cm⁻¹; 1H NMR (400 MHz, CDCl₃) δ 3.00 (s, 3H), 3.21 (s, 3H), 3.41 (s, 2H), 3.48—3.50 (m, 2H), 3.59—3.63 (m, 4H), 3.74—3.77 (m, 2H), 3.86—3.91 (m, 6H); 13C NMR (100 Hz, CDCl₃) δ 35.9, 37.3, 38.0, 41.4, 42.7, 47.5, 56.6, 51.6, 110.4 (m), 111.8 (m), 122.0 (t), 122.5 (t), 127.2 (t), 154.2, 155.1 (dd, J = 241 Hz, 155.2 (dd, J = 242 Hz), 155.8, 165.0, 167.0. HRMS calc'd for C₁₉H₁₇F₂N₃O: M⁺ 253.1027, found 253.1021. Anal. Calcd for C₁₉H₁₇F₂N₃O: C, 56.91; H, 5.17; N, 16.59 Found: C, 57.12; H, 5.29; N, 16.40.

1-Methyl-7-(2,6-diethylnitromethyleniminofuran-4,6-diones

1,2-Dihydropyrido[1,2-a]pyrimidin-1-ium-4-olate 14. (1-Methylamino)pyridine (119 mg, 1.1 mmol) in 15 mL of dry CH₂Cl₂ was injected onto the coldfinger containing 13 (obtained from Meldrum’s acid derivative 12 (349 mg, 1.0 mmol) as described above), and the resulting mixture was stirred for 24 h. The solvent was evaporated, and the crude product was purified by flash chromatography (silica gel, 5% MeOH/ether) to yield 180 mg (yield 59%) of a yellow solid: mp 157—158 °C; IR (KBr) ν 1717, 1636, 1617, 1559 cm⁻¹; 1H NMR (400 MHz, CDCl₃) δ 1.12 (t, J = 7.7 Hz, 6H), 3.08 (s, 3H), 3.26 (s, 2H), 3.63—3.69 (m, 3H); 13C NMR (100 Hz, CDCl₃) δ 34.3, 35.6, 36.6, 39.1, 111.5, 116.0, 125.9, 156.2 (dd, J = 252 Hz), 158.8, 165.8. Anal. Calcd for C₁₉H₁₇F₂N₃O: C, 57.98; H, 6.36; N, 15.60. Found: C, 57.95; H, 6.35; N, 15.40.

1-Methyl-7-(2,6-diethylnitromethyleniminofuran-4,6-diones

1,2-Dihydropyrido[1,2-a]pyrimidin-1-ium-4-olate 14. (1-Methylamino)pyridine (119 mg, 1.1 mmol) in 15 mL of dry CH₂Cl₂ was injected onto the coldfinger covered with iminoprodienone 8 (as described above), and the resulting mixture was stirred for 24 h. The solvent was evaporated, and the crude product was purified by flash chromatography (silica gel, 50% MeOH/ether) to yield 180 mg (yield 59%) of a yellow solid: mp 157—158 °C; IR (KBr) ν 1717, 1636, 1617, 1559 cm⁻¹; 1H NMR (400 MHz, CDCl₃) δ 1.12 (t, J = 7.7 Hz, 6H), 3.08 (s, 3H), 3.26 (s, 2H), 3.63 (s, 2H), 6.83—6.89 (m, 3H), 2.47—2.53 (m, 2H), 2.64 (s, 3H), 3.47 (s, 2H), 3.48—3.50 (m, 2H), 3.59—3.63 (m, 4H), 3.74—3.77 (m, 2H), 3.86—3.91 (m, 6H); 13C NMR (100 Hz, CDCl₃) δ 35.8, 37.1, 38.0, 49.4, 50.4, 111.3 (m), 122.0 (t), 127.2 (t), 155.2 (dd, J = 256 Hz), 156.3, 164.9. Anal. Calcd for C₁₉H₁₇F₂N₃O: C, 58.43; H, 5.62; N, 16.40. Found: C, 58.49; H, 5.59; N, 15.40.

1-Methyl-7-(2,6-diethylnitromethyleniminofuran-4,6-diones

1,2-Dihydropyrido[1,2-a]pyrimidin-1-ium-4-olate 14. (1-Methylamino)pyridine (119 mg, 1.1 mmol) in 15 mL of dry CH₂Cl₂ was injected onto the coldfinger containing 13 (obtained from Meldrum’s acid derivative 12 (349 mg, 1.0 mmol) as described above), and the resulting mixture was stirred for 24 h. The solvent was evaporated, and the crude product was purified by flash chromatography (silica gel, 50% MeOH/ether) to yield 180 mg (yield 59%) of a yellow solid: mp 157—158 °C; IR (KBr) ν 1717, 1636, 1617, 1559 cm⁻¹; 1H NMR (400 MHz, CDCl₃) δ 1.12 (t, J = 7.7 Hz, 6H), 3.08 (s, 3H), 3.26 (s, 2H), 3.63 (s, 2H), 6.83—6.89 (m, 3H), 2.47—2.53 (m, 2H), 2.64 (s, 3H), 3.47 (s, 2H), 3.48—3.50 (m, 2H), 3.59—3.63 (m, 4H), 3.74—3.77 (m, 2H), 3.86—3.91 (m, 6H); 13C NMR (100 Hz, CDCl₃) δ 35.8, 37.1, 38.0, 49.4, 50.4, 111.3 (m), 122.0 (t), 127.2 (t), 155.2 (dd, J = 256 Hz), 156.3, 164.9. Anal. Calcd for C₁₉H₁₇F₂N₃O: C, 58.43; H, 5.62; N, 16.40. Found: C, 58.49; H, 5.59; N, 15.40.
4-Methyl-7-[2-(6-diethylphenyl)iminomethyl]perhydro[1,4]diazepine-5-one 16. To iminopropadienone 13, obtained from 12 as above, was injected a solution of 81.5 mg (1.1 mmol) of N,N-dimethylhexamethyleneimine in 30 mL of dry THF, and the resulting mixture was stirred for 3 days. The solvent was evaporated and the crude product was purified by flash chromatography (silica gel, 5% MeOH/ether) to yield 70 mg (yield 26%) as a yellow oil: IR (KBr) 3340, 1646 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.13 (t, J = 7.7 Hz, 6H), 2.37–2.47 (m, 4H), 3.01 (s, 3 H), 3.43–3.71 (m, 4H), 3.82 (s, 2 H), 4.50 (br, 1H), 6.97 (t, J = 7.0 Hz, 1H), 7.06 (d, J = 0.0 Hz, 2H); ¹³C NMR (100 Hz, CDCl₃) δ 140.4, 24.5, 35.4, 43.8, 52.2, 123.2, 126.3, 134.7, 144.3, 150.9, 167.7. HRMS calc'd for C₁₇H₂₅N₃O: C, 71.02; H, 8.77; N, 14.40.

Matrix isolation of 2,6-Difluoropyrimidinylmonopropadienone 6 Generated from 6. 3-(2,6-Difluorophenyl)oxazolidine-5,4,4′-pyrimidine-4H-one 6 (10 mg, 0.04 mmol) was sublimed at 100 °C through the FVT tube at 700 °C with Ar matrix isolation of 8 on a BaF₂ disk at 8 K over the course of 10 min: IR (Ar, 8 K) 2247 vs, 2145 w, 2137 w, 1634, 1483 w, 1017 w, 778 w cm⁻¹. Also present were the following peaks: 3518 w, 3507 w, 2259 m, 770 m cm⁻¹ (hydrogen isocyanate, HNCO). FVT of Pyridopyrimidines. 2-tert-Butylphenyliminopropadienone 19a Generated from 2-((2-tert-Butylphenyl)amino)pyrido[1,2-a]pyrimidin-4-one 20a. Compound 20a (10 mg, 0.025 mmol) was sublimed at 140 °C through the FVT tube at 850 °C with Ar matrix isolation of 19a on a BaF₂ disk at 8 K over the course of 10 min: IR (Ar, 8 K) 2237 vs, 2138 w, 1624 m, 1354 w, 730 w cm⁻¹. Also present were the following peaks: 3535 w, 3429 w, 3074 w, 1611 s, 1608 s, 1575 w, 1484 w, 1445 w, 1317 w, 1273 w, 1149 w, 735 m cm⁻¹ (2-aminopyridine). Mesityliminopropadienone 19b Generated from 2-Mesitylaminopyrido[1,2-a]pyrimidin-4-one 20b. Compound 20b (10 mg, 0.025 mmol) was sublimed at 140 °C through the FVT tube at 850 °C with Ar matrix isolation of 19b on a BaF₂ disk at 8 K over the course of 10 min: IR (Ar, 8 K) 2240 vs, 2167 m, 1583 w, 1480 m, 792 w cm⁻¹; also present were the following peaks: 3535 w, 3429 w, 3074 w, 1611 s, 1608 s, 1575 w, 1484 w, 1445 w, 1317 w, 1273 w, 1149 w, 735 m cm⁻¹ (2-aminopyridine). FVT of Pyridopyrimidinium Olates. 2,6-Difluoropyrimidinylmonopropadienone 8 Generated from 1-Methyl-2-[(2,6-difluorophenyl)iminomethyl]-2,6-dihydropyrido[1,2-a]pyrimidine-4-olate 7a and 1-Methyl-4-[(2,6-difluorophenyl)iminomethyl]-2,6-dihydropyrido[1,2-a]pyrimidine-4-olate 7b. The 1:1 mixture of compounds 7a and 7b (10 mg, 0.031 mmol) was sublimed at 160 °C through the FVT tube at 550 °C with Ar matrix isolation of 8 on a BaF₂ disk at 8 K over the course of 10 min: IR (Ar, 8 K) 2247 vs, 2145 w, 2137 w, 1634 m, 1483 w, 1017 w cm⁻¹. Also present were the following peaks: 1612 s, 1602 s, 1578 w, 1524 m, 1511 m, 1459 m, 1421 m, 1336 w, 1289 m, 1156 m, 1074 m, 771 m, 734 w cm⁻¹ (2-(methylaminopyridine).

5-Amino-6,2-difluorophenyl-4-isoxazolocarboxamide was prepared by the method of Rajagopalan and Talaty. 2-Cyanocacetamide (1.68 g, 20.0 mmol) in 30 mL of absolute ethanol was added into a well-stirred solution of sodium ethoxide, which was prepared from 0.46 g (20.0 mmol) of sodium in 30 mL of absolute ethanol. The resulting suspension was stirred at 0 °C in an ice bath. 2,6-Difluorobenzhydrazinyl chloride (3.8 g, 20.0 mmol) in 30 mL of absolute ethanol was added slowly to the mixture, which was stirred for 15 min at 0 °C and then allowed to stir for another 90 min at room temperature. The mixture was then filtered for 2.5 h and was then hydrolyzed by pouring it onto 25 mL of crushed ice. The precipitate was filtered off and recrystallized from methanol/water to afford 1.3 g (27%): mp 174–176 °C; ¹H NMR (200 MHz, MeOD) δ 5.02 (s, 2H), 6.42 (s, 2H), 7.05–7.728 (m, 2 H), 7.53–7.65 (m, 1H); ¹³C NMR (100 Hz, MeOD) δ 88.5, 106.7 (t, J = 12.0 m, 132.7 t, 151.1, 159.9 (dd, J = 250 Hz), 163.3, 170.8.

2-(Methylaminopyridine) 2-(Methylaminopyridine). IR (Ar, 8 K) 3535 m, 3429 m, 3074 w, 3031 w, 1611 v, 1608 vs, 1576 w, 1575 m, 1497 w, 1484 s, 1445 s, 1317 m, 1273 w, 1149 w, 987 w, 803 v, 785 w, 772 w, 765 w, 735 w, 519 w cm⁻¹. Sublimation temperature 150 °C. 2-(2-Methylaminopyridine) 2-(2-Methylaminopyridine) 2-(2-Methylaminopyridine)
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1511 s, 1493 w, 1464 w, 1459 m, 1440 w, 1429 w, 1421 s, 1414 m, 1336 m, 1329 w, 1289 m, 1169 w, 1156 w, 1149 w, 1131 w, 1089 w, 1074 w, 981 w, 771 s, 734 w, 522 w cm⁻¹. Sublimation temperature 10 °C.

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**Supporting Information Available:** Experimental procedures for the preparation of the dimethoxyphenyliminopropadienones; IR spectra of diethyliminopropadienone (Ar matrix and calculated (B3LYP/6-31G**)), Figure S1), mesityliminopropadienone (Ar matrixes, Figure S2), and dimethoxyphenyliminopropadienones (Ar matrixes and neat films, Figures S3–S4); X-ray data for pyridopyrimidinium olate 7a (Figure S5 and Tables S1–S5); Cartesian coordinates, energies, and calculated IR spectra of 8, 13, 19a, 23, and 24. This material is available free of charge via the Internet at http://pubs.acs.org.

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