The Reaction of Imidazo[1,5-*a*]pyridines with Methyl- and Phenyltriazolinediones and with Diethyl Azodicarboxylate

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Imidazo[1,5-*a*]pyridines react in one of two ways with methyl- and phenyl triazolinediones and diethyl azodicarboxylate to give either Michael type addition products at C-3 or C-1, or novel 1,2,4-triazolines. The nature of the product depends upon the dienophile and the substitution pattern of the imidazo[1,5-*a*]pyridine.

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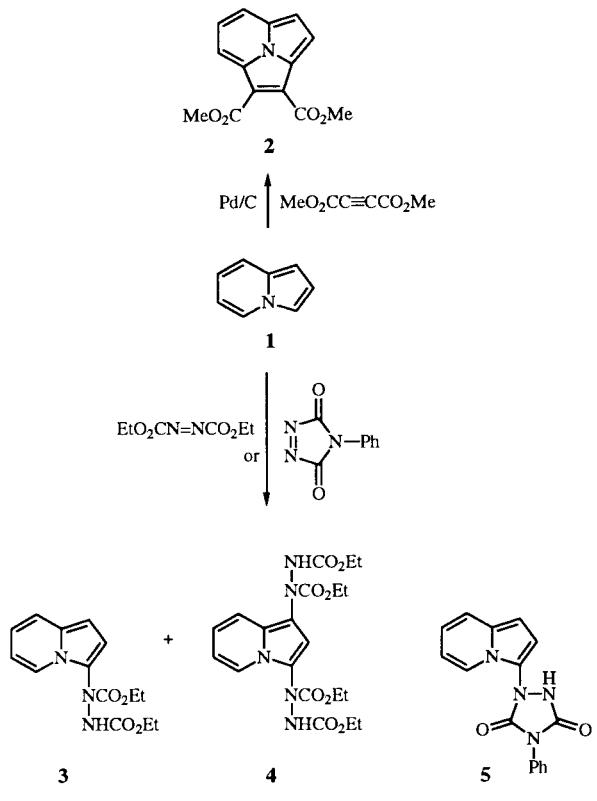
The cycloaddition of indolizine **1** with dimethyl acetylenedicarboxylate, in the presence of a dehydrogenation catalyst, has been shown [1,2] to give the cycloadduct **2** (Scheme 1). In contrast, reaction of **1** with diethyl azodicarboxylate and phenyl triazolinedione provides the Michael type addition products **3**, **4** and **5** [3,4].

We describe in this paper the reaction of imidazo[1,5-*a*]-pyridines with phenyl- and methyltriazolinedione and diethyl azodicarboxylate to yield adducts of unexpected structure.

Scheme 1



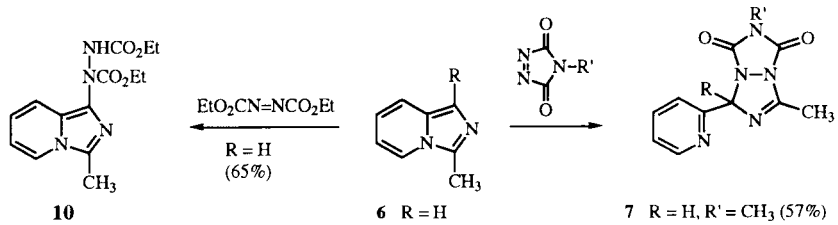
Results.

3-Methylimidazo[1,5-*a*]pyridine **6** reacted instantaneously at room temperature with methyltriazolinedione to yield a 1:1 adduct **7** in 57% yield (after recrystallization). Examination of the infra red spectrum of **7** indicated the absence of an NH group thus eliminating the formation of a Michael type adduct. The nmr spectrum of **7** revealed the presence of a 2-substituted pyridine ring with characteristic peaks at δ 8.65 for H-6. In addition to the N-CH_3 singlet at δ 3.10 there was a methyl doublet at δ 2.46 (J = 1.2 Hz) coupled to a one proton quartet at δ 6.61. The assignment of this spectral data to the triazolotriazoline **7** was confirmed by an X-ray structure of **7**. In a similar fashion, 1-acetyl-3-methylimidazo[1,5-*a*]pyridine **8** reacted with phenyl triazolinedione to afford the 1:1 adduct **9** in 91% yield (Scheme 2). The nmr spectrum of **9** again showed the characteristic low field signal (δ 8.72) for H-6 of the pyridine ring.

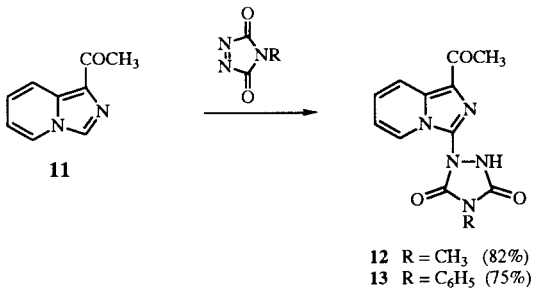
The reaction of **6** with diethyl azodicarboxylate followed a different course affording the Michael type adduct **10** in 65% yield. The structure of **10** was apparent from the infrared spectrum which exhibited an NH at 3148 cm^{-1} plus C=O stretches at 1742 and 1720 cm^{-1}. The nmr spectrum confirmed the loss of C1-H of **6** at δ 7.30 and the appearance of an NH at δ 9.57 in **10**.

Reaction of 1-acetylimidazo[1,5-*a*]pyridine **11** with either methyl- or phenyltriazolinedione gave the 1:1

Scheme 2



Scheme 3



11

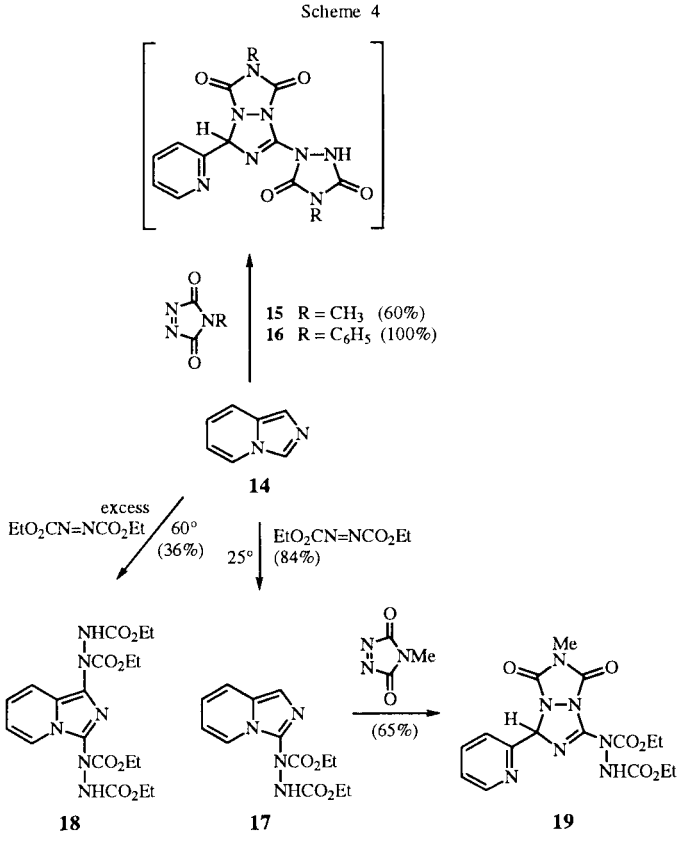
12 R = CH_3 (82%)
13 R = C_6H_5 (75%)

Michael adducts **12** and **13** rather than triazolotriazolines (as with **6** and **8**) (Scheme 3).

The assignment of structures to **12** and **13** followed from the appearance of NH bands in the infrared spectrum and the loss of the C3-H proton of **11** at δ 8.08 in the nmr spectrum in addition to the emergence of an NH peak at *ca.* δ 11.30.

When methyl- and phenyltriazolinedione reacted with the unsubstituted imidazo[1,5-*a*]pyridine **14**, 2:1 adducts were formed. Their structures have been tentatively assigned as triazolotriazolines **15** and **16** based upon their nmr spectra (Scheme 4). Both have low field doublets (δ 8.50 and δ 8.55 respectively for the C6-H pyridine proton) plus singlets at δ 6.64 and δ 6.63 respectively for the 1,2,4-triazole ring proton. These 2:1 adducts could not be satisfactorily purified and they appeared to decompose on silica gel chromatography. Their structural assignments are based upon nmr comparisons with other triazolotriazolines **7** and **9**.

Scheme 4



15 R = CH_3 (60%)
16 R = C_6H_5 (100%)

14

excess $EtO_2CN{=}NCO_2Et$, 60° (36%)

25° $EtO_2CN{=}NCO_2Et$ (84%)

(65%)

18 **17** **19**

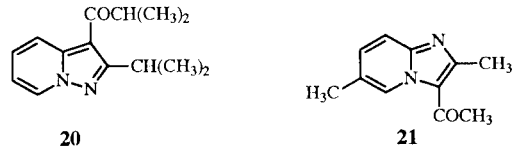
When the unsubstituted ring system **14** reacted with diethyl azodicarboxylate, the Michael type adduct **17** was formed wherein addition had taken place at the 3-position. This was evident from the loss of the 3-proton in **17** at δ 8.05 (the 1-proton [5] is at δ 7.39). When excess diethyl azodicarboxylate was used and the reaction heated in refluxing chloroform then the *bis*-Michael type adduct **18** was formed. The second molecule of diethyl azodicarboxylate reacted at the 1-position.

When the mono diethyl azodicarboxylate adduct **17** was allowed to react with methyltriazolinedione then the triazolotriazoline **19** was formed as evidenced from the nmr spectrum. The characteristic one proton singlet at δ 6.63 and the low field doublet at δ 8.56 were both present.

No reaction occurred between the 3-methylimidazo-[1,5-*a*]pyridine **6** and *N*-methylmaleimide even in refluxing xylene. The reaction of **6** with dimethyl acetylenedicarboxylate was extremely colorful at room temperature. The reaction mixture turned almost black immediately, but tlc revealed a multitude of rainbow colored materials including unreacted **6**.

No reaction was observed between the pyrazolo[1,2-*a*]-pyridine **20** [6] or the imidazo[1,2-*a*]pyridine **21** [7] with phenyl triazolinedione at room temperature (Scheme 5).

Scheme 5

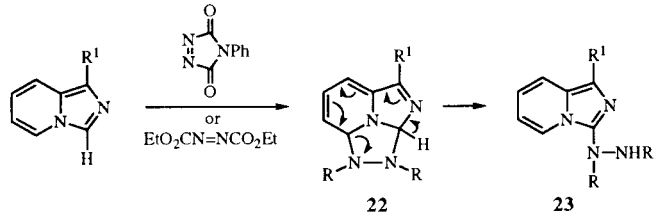


20 **21**

Mechanisms.

There are several mechanisms that may be operating in the above reactions. A possible first step in the reaction of both phenyltriazolinedione and diethyl azodicarboxylate with imidazo[1,5-*a*]pyridines containing a hydrogen in position 3, is an [8+2] cycloaddition to give intermediate **22** (Scheme 6).

Scheme 6

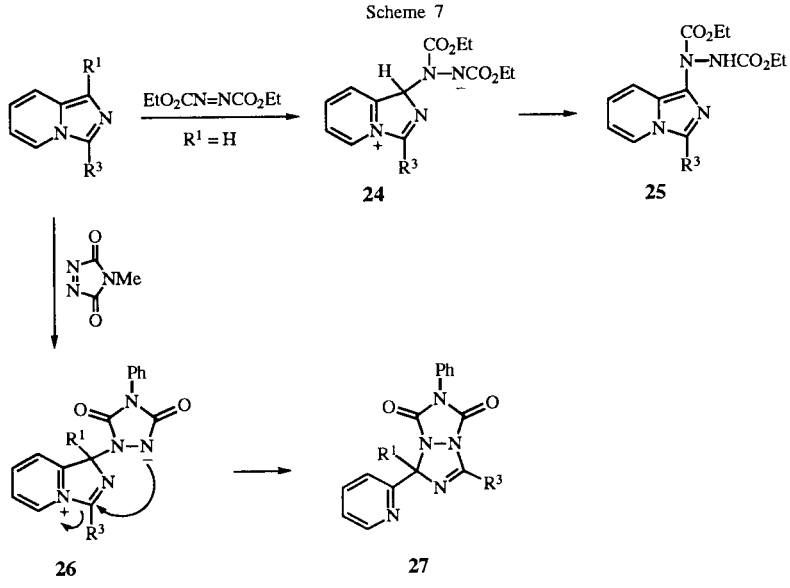


or $EtO_2CN{=}NCO_2Et$

22 **23**

Such cycloadditions have been observed [9] with phenyl triazolinedione and diethyl azodicarboxylate with

Scheme 7



the 3*aH*-indene system, the carbocyclic analog of imidazo[1,5-*a*]pyridine.

A [1,9] *H*-shift in **22** then affords the 3-substituted products **23**. When the 3-position is blocked then electrophilic addition takes place at the 1-position to give intermediate **24** (Scheme 7) which undergoes a proton shift to give products **25**.

Addition of phenyltriazolinedione at the 1-position leads to intermediate **26** which undergoes a different rearrangement as shown to provide products **27**. The driv ing force for this alternative pathway is the aromatization of the pyridine ring.

X-ray Study of 2,7-Dimethyl-5-(2-pyridinyl)-1*H*, 5*H*-[1,2,4]triazolo[1,2-*a*] [1,2,4]triazole-1,3(2*H*)-dione (**7**).

Fractional coordinates, bond lengths and other parameters are listed in Tables 1-5. An ORTEP diagram is shown in Figure 1.

The bond lengths and bond angles of **7** and the bend along the N2-N4 bond of 41.36(.12) versus 39.14 agrees well with 7-(methylthio)-2,5,5-trimethyl-1*H*,5*H*-[1,2,4]-triazolo[1,2-*a*][1,2,4]triazole-1,3(2*H*)-dione [10]. A similar bend along the N2-N4 bond of 39.6° with an adduct of 5-methoxy-4-methyl-2-(*p*-tolyl)oxazole [11] was observed; but, our structure shows a slightly longer C7-C10 bond of 1.52 versus 1.46Å in the oxazole.

EXPERIMENTAL

2,7-Dimethyl-5-(2-pyridinyl)-1*H*, 5*H*-[1,2,4]triazolo[1,2-*a*]-[1,2,4]triazole-1,3(2*H*)-dione (**7**).

Nitrogen dioxide was passed into a cold (0°) slurry of *N*-methylurazole (2.3 g, 20 mmoles) and anhydrous sodium sul-

Table 1

Fractional Coordinates (x10^4) aknd B_{eq}(Å^2) for **7**
Estimated Standard Deviations are in Parentheses

$B_{eq} = 4/3(a^2B_{11}+b^2B_{22}+c^2B_{33}+ab\cos\gamma B_{12}+ac\cos\beta B_{13}+bc\cos\alpha B_{23})$

	x	y	z	B_{eq}
N(1)	15209(2)	7282(4)	3551(1)	1.30(8)
C(1)	16895(2)	7935(5)	4392(1)	1.82(10)
C(2)	14339(2)	8544(5)	2821(1)	1.48(10)
O(2)	14797(2)	10207(3)	2725(1)	1.73(7)
N(3)	12719(2)	7537(4)	2196(1)	1.21(8)
C(4)	11840(2)	6688(5)	1383(1)	1.36(10)
C(5)	11759(3)	8193(5)	856(1)	1.62(10)
N(6)	11167(2)	4660(4)	1192(1)	1.26(8)
C(7)	11544(2)	3833(4)	1902(1)	1.30(10)
N(8)	12710(2)	5631(4)	2577(1)	1.28(8)
C(9)	14315(2)	5315(5)	3396(1)	1.47(10)
O(9)	14809(2)	3740(3)	3881(1)	1.89(7)
C(10)	9929(2)	3704(4)	1616(1)	1.29(10)
C(11)	9394(3)	5561(5)	1735(2)	1.68(11)
C(12)	7835(3)	5384(5)	1393(2)	1.93(11)
C(13)	6901(3)	3370(5)	949(2)	1.89(11)
C(14)	7555(3)	1591(5)	875(2)	1.92(11)
N(15)	9051(2)	1712(4)	1198(1)	1.60(8)

Table 1a

Fractional Coordinates (x 10^3) and Isotropic Temperature Factors for Hydrogen Atoms for **7**

	x	y	z	B_{iso}
H(1A)	1760	836	433	2.0
H(1B)	1740	656	479	2.0
H(1C)	1681	931	461	2.0
H(5A)	1110	736	30	2.2
H(5B)	1292	851	116	2.2
H(5C)	1119	971	73	2.2
H(7)	1210	224	210	1.8
H(11)	1010	700	205	2.0
H(12)	740	669	146	2.4
H(13)	576	320	68	2.2
H (14)	687	12	56	2.3

Table 2

Bond Lengths(A) and Angles (°) for **7**

A. Bond Lengths(Å)

N(1)-C(1)	1.469(3)	C(7)-N(8)	1.482(3)
N(1)-C(2)	1.379(3)	C(7)-C(10)	1.524(1)
N(1)-C(9)	1.398(3)	N(8)-C(9)	1.381(3)
C(2)-O(2)	1.204(2)	C(9)-O(9)	1.206(3)
C(2)-N(3)	1.412(2)	C(10)-C(11)	1.378(3)
N(3)-C(4)	1.424(3)	C(10)-N(15)	1.341(3)
N(3)-N(8)	1.421(2)	C(11)-C(12)	1.393(1)
C(4)-C(5)	1.470(3)	C(12)-C(13)	1.376(4)
C(4)-N(6)	1.278(3)	C (13)-C(14)	1.379(3)
N(6)-C(7)	1.469(2)	C(14)-N(15)	1.342(1)

B. Bond Angles(°)

C(1)-N(1)-C(2)	123.2(2)	N(8)-C(7)-C(10)	111.6(1)
C(1)-N(1)-C(9)	124.4(2)	N(3)-N(8)-C(7)	106.6(2)
C(2)-N(1)-C(9)	112.4(2)	N(3)-N(8)-C(9)	108.9(1)
N(1)-C(2)-O(2)	129.0(2)	C(7)-N(8)-C(9)	128.5(2)
N(1)-C(2)-N(3)	104.7(2)	N(1)-C(9)-N(8)	104.8(2)
O(2)-C(2)-N(3)	126.3(2)	N(1)-C(9)-O(9)	127.9(2)
C(2)-N(3)-C(4)	126.0(1)	N(8)-C(9)-O(9)	127.3(2)
C(2)-N(3)-N(8)	108.0(2)	C(7)-C(10)-C(11)	121.8(2)
C(4)-N(3)-N(8)	105.3(2)	C(7)-C(10)-N(15)	113.9(2)
N(3)-C(4)-C(5)	118.6(2)	C(11)--C(10)-N(15)	124.2(1)
N(3)-C(4)-N(6)	114.0(2)	C(10)--C(11)-C(12)	118.3(2)
C(5)-C(4)-N(6)	127.3(2)	C(11)-C(12)-C(13)	118.5(2)
C(4)-N(6)-C(7)	108.6(2)	C(12)--C(13)-C(14)	118.9(1)
N(6)-C(7)-N(8)	104.5(2)	C(13)--C(14)-N(15)	123.9(1)
N(6)-C(7)-C(10)	109.5(2)	C(10)--N(15)-C(14)	116.2(2)

Table 3

Torsion Angles(°)for **7**

C(1)-N(1)-C(2)-O(2)	5.2(3)	C(4)-N(6)-C(7)-N(8)	-5.9(2)
C(1)-N(1)-C(2)-N(3)	-171.8(1)	C(4)-N(6)-C(7)-C(10)	113.8(2)
C(9)-N(1)-C(2)-O(2)	-174.0(2)	N(6)-C(7)-N(8)-N(3)	9.8(1)
C(9)-N(1)-C(2)-N(3)	9.0(2)	N(6)-C(7)-N(8)-C(9)	-122.0(1)
C(1)-N(1)-C(9)-N(8)	168.8(1)	C(10)-C(7)-N(8)-N(3)	-108.4(2)
C(1)-N(1)-C(9)-O(9)	-8.2(2)	C(10)-C(7)-N(8)-C(9)	119.7(2)
C(2)-N(1)-C(9)-N(8)	-12.0(2)	N(6)-C(7)-C(10)-C(11)	-93.1(3)
C(2)-N(1)-C(9)-O(9)	170.9(2)	N(6)-C(7)-C(10)-N(15)	82.8(2)
N(1)-C(2)-N(3)-C(4)	-127.8(2)	N(8)-C(7)-C(10)-C(11)	22.1(3)
N(1)-C(2)-N(3)-N(8)	-2.3(2)	N(8)-C(7)-C(10)-N(15)	-162.0(2)
O(2)-C(2)-N(3)-C(4)	55.1(3)	N(3)-N(8)-C(9)-N(1)	10.0(2)
O(2)-C(2)-N(3)-N(8)	-179.4(2)	N(3)-N(8)-C(9)-O(9)	-173.0(2)
C(2)-N(3)-C(4)-C(5)	-48.1(3)	C(7)-N(8)-C(9)-N(1)	141.0(1)
C(2)-N(3)-C(4)-N(6)	133.4(2)	C(7)-N(8)-C(9)-O(9)	-41.9(2)
N(8)-N(3)-C(4)-C(5)	-174.7(1)	C(7)-C(10)-C(11)-C(12)	174.6(2)
N(8)-N(3)-C(4)-N(6)	6.8(2)	N(15)-C(10)-C(11)-C(12)	-0.8(4)
C(2)-N(3)-N(8) -C(7)	-147.0(1)	C(7) -C(10)-N(15)-C(14)	-175.0(2)
C(2)-N(3)-N(8)-C(9)	-5.0(2)	C(11)-C(10)-N(15)-C(14)	0.7(3)
C(4)-N(3)-N(8)-C(7)	-10.0(1)	C(10)-C(11)-C(12)-C(13)	-0.3(4)
C(4)-N(3)-N(8)-C(9)	132.0(1)	C(11)-C(12)-C(13)-C(14)	1.3(4)
N(3)-C(4)-N(6)-C(7)	-0.4(2)	C(12)-C(13)-C(14)-N(15)	-1.4(4)
C(5)-C(4)-N(6)-C(7)	-178.7(1)	C(13)-C(14)-N(15)-C(10)	0.3(3)

Table 4

Close Intermolecular Contacts Between Non-hydrogen Atoms for **7**
Symmetry Operations Listed were Performed On the First Atom.
Distances are in Å.

O(2).....C(7)	x,	y-1,	z	3.465(2)
O(2).....O(9)	x,	y-1,	z	3.421(2)
O(9).....C(14)	x-1,	1/2-y,	z-1/2	3.151(3)
C(9).....C(13)	2-x,	y-1/2,	1/2-z	3.354(2)
C(12).....O(9)	2-x,	y-1/2,	1/2-z	3.356(2)
O(2).....N(1)	3-x,	y-1/2,	1/2-z	3.286(2)
O(2).....C(2)	3-x,	y-1/2,	1/2-z	2.918(2)
O(2).....O(2)	3-x,	y-1/2,	1/2-z	3.199(2)
O(2).....N(3)	3-x,	y-1/2,	1/2-z	3.181(1)
O(2).....C(4)	3-x,	y-1/2,	1/2-z	2.972(2)
O(2).....C(5)	3-x,	y-1/2,	1/2-z	3.232(3)
O(2).....N(6)	3-x,	y-1/2,	1/2-z	3.426(1)
C(5).....C(1)	3-x,	y-1/2,	1/2-z	3.428(3)

Table 5

Anisotropic Thermal Parameters (x10^4) for **7**

The expression is of the form:

$$\exp(-B_{11}h^2-B_{22}k^2-B_{33}l^2-B_{12}hk-B_{13}hl-B_{23}kl)$$

Estimated Standard Deviations are in Parentheses

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	42(2)	13(1)	11(1)	-17(7)	30(2)	-5(4)
C(1)	48(3)	17(1)	13(1)	-30(9)	28(3)	-18(5)
C(2)	51(3)	12(1)	16(1)	5(8)	43(3)	-18(5)
O(2)	63(2)	12(1)	17(1)	-32(6)	46(2)	-2(3)
N(3)	49(3)	10(1)	10(1)	-6(7)	33(2)	3(4)
C(4)	39(3)	15(1)	12(1)	26(8)	32(3)	1(5)
C(5)	60(3)	16(1)	11(1)	8(9)	37(3)	11(5)
N(6)	45(3)	14(1)	11(1)	-5(7)	38(3)	-7(4)
C(7)	51(3)	10(1)	14(1)	-19(8)	40(3)	-20(5)
N(8)	48(3)	11(1)	11(1)	-21(7)	34(3)	-2(4)
C(9)	51(3)	16(1)	13(1)	-6(8)	41(3)	-17(5)
O(9)	62(2)	18(1)	15(1)	-8(6)	42(2)	15(4)
C(10)	47(3)	12(1)	11(1)	11(8)	33(3)	14(5)
C(11)	65(3)	12(1)	17(1)	-9(8)	50(3)	0(5)
C(12)	79(3)	20(1)	20(1)	68(9)	69(4)	28(6)
C(13)	53(3)	23(1)	15(1)	8(9)	44(3)	33(6)
C(14)	64(3)	18(1)	14(1)	-62(9)	41(3)	4(5)
N(15)	58(3)	12(1)	16(1)	-28(7)	44(3)	-7(4)

fate (20 g) in methylene chloride (100 ml) until all the urazole was dissolved. The sodium sulfate was removed by filtration and the red filtrate concentrated to about half its volume on a rotary evaporator at room temperature. To this solution was added 3-methylimidazo[1,5-*a*]pyridine (**6**) [8] in portions (1.8 g, 13.6 mmoles) until only a faint red color remained. The solvent was removed *in vacuo* and the residue recrystallized twice from acetone-hexane to give white needles, 1.91 g (57%), mp 121-123°; ^{1}H nmr (deuteriochloroform): δ 2.46 (d, J = 1.2 Hz, 3H), 3.10 (s, 3H), 6.61 (q, J = 1.2 Hz, 1H), 7.30 (ddd, J = 7.6, 5.0, 1.4 Hz, 1H, pyridine H5), 7.47 (dt, J = 7.5, 1.4, 0.9 Hz, 1H, pyridine H3), 7.76 (dt, J = 7.6, 7.5, 2.0 Hz, 1H, pyridine H4), 8.65 (ddd, J = 5.0, 2.0, 0.9 Hz, 1H, pyridine H6); ir: 1720 cm^{-1}; ms: m/z 245.

Anal. Calcd. for $C_{11}H_{11}N_5O_2$: C, 53.87; H, 4.52; N, 28.56. Found: C, 53.88; H, 4.59; N, 28.49.

5-Acetyl-7-methyl-2-phenyl-5-(2-pyridinyl)-1*H*,5*H*-[1,2,4]triazolo[1,2-*a*][1,2,4]triazole-1,3(2*H*)-dione (**9**).

A mixture of 1-acetyl-3-methylimidazo[1,5-*a*]pyridine (**8**) [8] (1.0 g, 5.74 mmoles) and 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione (1.1 g, 6.28 mmoles) in chloroform (10 ml) was stirred at room temperature for 1 hour. The solvent was evaporated and the residue recrystallized from acetone-hexane to give white nee-

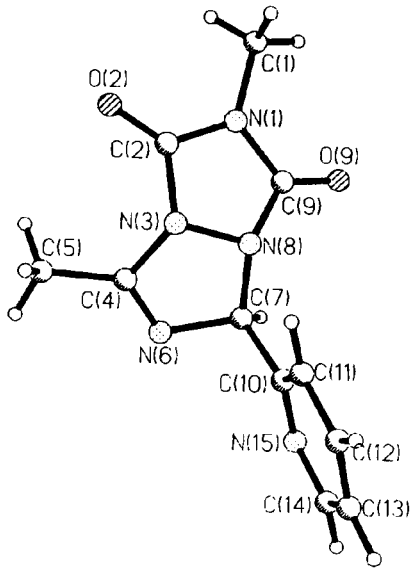


Figure 1. ORTEP Drawing of **7**.

dles, 1.83 g (91%), mp 143-145°; ^{1}H nmr (deuteriochloroform): δ 2.30 (s, 3H), 2.52 (s, 3H), 7.20-7.65 (m, 6H), 7.65-7.95 (m, 2H), 8.72 (d, J = 4 Hz, 1H); ir: 1736 cm^{-1}; ms: m/z 349.

Anal. Calcd. for $C_{18}H_{15}N_5O_3$: C, 61.89; H, 4.33; N, 20.05. Found: C, 62.16; H, 4.42; N, 20.00.

1-(3-Methylimidazo[1,5-*a*]pyridin-1-yl]-1,2-hydrazinedicarboxylic Acid Diethyl Ester (**10**).

Diethyl azodicarboxylate (1.84 g, 10.6 mmoles) and 3-methylimidazo[1,5-*a*]pyridine (**6**) (1.32 g, 10.0 mmoles) were stirred in methylene chloride (15 ml) for 18 hours. The solvent was removed and the product recrystallized from ethanol as white crystals, 2.0 g (65%), mp 205-207° dec. ^{1}H nmr (deuteriochloroform): δ 1.16 (t, J = 7 Hz, 3H), 1.24 (t, J = 7 Hz, 3H), 2.64 (s, 3H), 4.17 (q, J = 7 Hz, 4H), 6.40-6.90 (m, 2H), 7.58 (d, J = 7.5 Hz, 1H), 7.75 (bd, d, J = 8 Hz, 1H), 9.57 (bd, s, NH); ir: 3148, 1742, 1720 cm^{-1}; ms: m/z 306.

Anal. Calcd. for $C_{14}H_{18}N_4O_4$: C, 54.89; H, 5.92; N, 18.29. Found: C, 54.70; N, 5.55; N, 18.31.

1-(1-Acetylimidazo[1,5-*a*]pyridin-3-yl)-4-methyl-1,2,4-triazolidine-3,5-dione (**12**).

To a solution of 4-methyl-1,2,4-triazoline-3,5-dione (prepared as for **7**) was added 1-acetylimidazo[1,5-*a*]pyridine (**11**) [8] in portions (2.5 g, 15.6 mmoles) until only a faint red color remained. The precipitated solid, 3.5 g (82%) was recrystallized from methanol as white needles, mp 261-262° dec.; ^{1}H nmr (DMSO-d_6): δ 2.56 (s, 3H), 3.10 (s, 3H), 7.24 (m, 1H), 7.56 (m, 1H), 8.35 (d, J = 9.5 Hz, 1H), 8.58 (d, J = 7.5 Hz, 1H); ir: 3142 (w, bd), 1712 cm^{-1}; ms: m/z 273.

Anal. Calcd. for $C_{12}H_{11}N_5O_3$: C, 52.75; H, 4.06; N, 25.63. Found: C, 52.52; H, 4.09; N, 25.53.

1-(1-Acetylimidazo[1,5-*a*]pyridin-3-yl)-4-phenyl-1,2,4-triazolidine-3,5-dione (**13**).

4-Phenyl-3*H*-1,2,4-triazoline-3,5-dione (0.56 g, 3.20 mmoles) was added in portions to a stirred solution of 1-acetylimidazo[1,5-*a*]pyridine (**11**) (0.50 g, 3.12 mmoles) in methylene chloride (10 ml) until a faint red color remained. The resultant precipitate was filtered and recrystallized from acetone to give fine white needles, 0.78 g (75%), mp 271-273° dec.; ^{1}H nmr (DMSO-d_6): δ 2.57 (s, 3H), 6.90-7.80 (m, 7H), 8.24 (m, 1H), 8.63 (m, 1H); ir: 3144 (bd, w), 1719 cm^{-1}; ms: m/z 335.

Anal. Calcd. for $C_{17}H_{13}N_5O_3$: C, 60.89; H, 3.91; N, 20.89. Found: C, 60.64; H, 4.02; N, 20.61.

Formation of Triazolotriazoline (**15**).

To a solution of 4-methyl-1,2,4-triazoline-3.5-dione (prepared as for **7**) was added imidazo[1,5-*a*]pyridine (**14**) [8] (1.15 g, 9.7 mmoles) portionwise until a faint red color still remained. The solvent was evaporated to leave crude **15** as a hard brown foam (2.0 g, 60%); ^{1}H nmr (deuteriochloroform): δ 3.03 (s, 3H), 3.07 (s, 3H), 6.64 (s, 1H), 7.27 (m, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.70 (dt, J = 8.0, 1.0 Hz, 1H), 8.50 (d, J = 5.0 Hz, 1H), 9.06 (bd, NH).

Attempted chromatography of this material over silica gel eluting with 2% methanol-chloroform resulted in decomposition.

Formation of Triazolotriazoline **16**.

Imidazo[1,5-*a*]pyridine (**14**) (0.55 g, 4.65 mmoles) was added in portions to a stirred solution of 4-phenyl-3*H*-1,2,4-triazoline-3,5-dione (1.75 g, 10.0 mmoles) in methylene chloride (10 ml), until only a faint red color remained. The mixture was filtered and the solvent evaporated to afford crude **16** as a hard brown foam, 2.21 g (100%); ^{1}H nmr (deuteriochloroform): δ 6.63 (s, 1H), 6.95-7.80 (m, 13H), 8.55 (d, J = 4.5 Hz, 1H), 8.63 (bd, NH).

Chromatography of this material over silica gel eluting with 2-4% methanol-chloroform resulted in decomposition.

1-Imidazo[1,5-*a*]pyridin-3-yl-1,2-hydrazinedicarboxylic Acid Diethyl Ester (**17**).

Diethyl azodicarboxylate (1.84 g, 10.6 mmoles) was added dropwise to a stirred solution of imidazo[1,5-*a*]pyridine (**14**) (1.18 g, 10.0 mmoles) in methylene chloride (15 ml). Stirring was continued for 18 hours when the solvent was evaporated. The residue was recrystallized from acetone-hexane to give white prisms, 2.45 g (84%), mp 163-165°; ^{1}H nmr (deuteriochloroform): δ 1.20 (t, J = 7 Hz, 3H), 1.33 (t, J = 7 Hz, 3H), 4.23 (q, J = 7 Hz, 4H), 6.50-6.95 (m, 2H), 7.25-7.55 (m, 1H), 7.40 (s, 1H), 8.48 (bd, d, J = 5.5 Hz, 1H), 10.48 (bd, NH); ir: 3169, 1755, 1739, 1721 cm^{-1}; ms: m/z 292.

Anal. Calcd. for $C_{13}H_{16}N_4O_4$: C, 53.42; H, 5.52; N, 19.17. Found: C, 53.22; H, 5.51; N, 19.04.

1,1'-Imidazo[1,5-*a*]pyridine-1,3-diyl*bis*-1,2-hydrazinedicarboxylic Acid Tetraethyl Ester (**18**).

Diethyl azodicarboxylate (7.25 g, 41.6 mmoles) and imidazo[1,5-*a*]pyridine (**14**) (1.0 g, 8.5 mmoles) were heated under reflux in chloroform (20 ml) for 6 hours. After cooling, the solvent was evaporated to leave a pale lavender solid. The solid was stirred with ether (25 ml) and filtered. Recrystallization from ethanol gave white crystals, 1.45 g (36%), mp 216-218° dec; ^{1}H nmr (DMSO-d_6): δ 0.90-1.35 (m, 12H), 3.90-4.35 (m, 8H), 6.65-7.10 (m, 2H), 7.57 (bd, d, J = 8.5 Hz, 1H), 8.19 (bd, d, J = 6.5 Hz, 1H), 10.10 (s, NH), 10.40 (s, NH); ir: 3293, 3171, 1758, 1739, 1721, 1709 cm^{-1}; ms: m/z 466.

Anal. Calcd. for $C_{19}H_{26}N_6O_8$: C, 48.92; H, 5.62; N, 18.02. Found: C, 48.91; H, 5.74; N, 17.91.

1-[6,7-Dihydro-6-methyl-5,7-dioxo-1-(2-pyridinyl)-1*H*,5*H*-[1,2,4]triazolo[1,2-*a*][1,2,4]triazol-3-yl]-1,2-hydrazinedicarboxylic Acid Diethyl Ester (**19**).

A solution of 4-methyl-1,2,4-triazoline-3,5-dione (prepared from *N*-methylurazole (0.80 g, 6.95 mmoles) as for **7**) was added dropwise to 1-imidazo[1,5-*a*]pyridin-3-yl-1,2-hydrazinedicarboxylic acid diethyl ester (**17**) (1.0 g, 3.43 mmoles) in methylene chloride (10 ml) until only a faint red color remained. The solvent was evaporated and the residue chromatographed over silica gel (125 g) eluting with 40% acetone-hexane. A hard white foam was obtained, 0.90 g (65%); ^{1}H nmr (deuteriochloroform): δ 1.20 (m, 6H), 3.00 (s, 3H), 4.20 (m, 4H), 6.63 (s, 1H), 7.22 (m, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.70 (dt, J = 8.0, 1.5 Hz, 1H), 8.04 (bd, NH), 8.56 (d, J = 4.5 Hz, 1H); ir: 3299, 1732 cm^{-1}; ms: m/z 405.

Anal. Calcd. for $C_{16}H_{19}N_7O_6$: C, 47.41; H, 4.72; N, 24.19. Found: C, 47.26; H, 4.93; N, 24.12.

X-ray Study of compound **7**.

Crystal Data: $C_{11}H_{11}O_2N_5$, Mr = 245.24, monoclinic, $P2_1/c$, a = 12.232(1), b = 5.658(1), c = 24.097(4)Å, β = 139.31(1)°, V = 1087.3(5)Å^3, Z = 4, D_c = 1.50 gm/cm^3, CuKα, λ = 1.5418, μ(CuKα) = 8.0 cm^{-1}, T = 123K, R = 0.038 for 1103 unique reflections.

A clear prism of compound **7** with dimensions 0.11 x 0.17 x 0.30 mm, was used for intensity measurements on a Siemens $P2_1$ diffractometer controlled by a Harris computer. CuKα radiation and a graphite monochromator were used for intensity measurement. The step-scan technique was used with a scan rate of 2°/min, a scan width of 3.4°, and a $2\theta_{max}$=136°. Ten reflections periodically monitored showed no loss of intensity during the data collection. Of the 1103 reflections unique reflections measured, 978 had intensities > 3σ. Standard deviations in the intensities were approximated by the equation:

$$\sigma^2(\mathbf{I}) = \sigma^2(\mathbf{I})\text{counting statistics} + (0.009\ \mathbf{I})^2$$

where the coefficient of **I** was calculated from the variations in intensities of the monitored reflections. Unit cell parameters were determined accurately by least squares fit of CuKα_1 2θ values (λ(Cu Kα_1)=1.5402) for 25 high 2θ reflections [12]. Lorentz and polarization corrections appropriate for a monochromator with 50% perfect character were applied and no intensity correction for absorption. The structure was obtained by direct methods, using DIREC [13]. Hydrogen atoms found in difference maps were very close to positions generated using planar or tetrahedral geometry, so generated positions were used. The structure was refined by least squares with the coordinates and anisotropic thermal parameters for nonhydrogen atoms included in the refinement. Isotropic thermal parameters for hydrogen atoms were set 1/2 unit higher than the isotropic equivalent of the thermal parameters of the attached heavier atom. The function minimized in the refinement was $\Sigma w(F_o^2-F_c^2)^2$, where weights w were $1/\sigma^2(F_o^2)$. Atomic form factors were from Doyle & Turner [14], except, for hydrogen which was from Stewart, Davidson & Simpson [15]. In the final refinement cycle, all shifts were <0.35σ. The final R was 0.038, and the standard deviation of fit was 4.22. A final difference map showed no peaks >0.18eÅ^{-3}. The CRYM system of computer programs was used [16].

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