scan–background technique, 2158 unique intensity data were recorded within the range $0 \leq 2\theta \leq 50°$. The 1784 reflections with $I \geq 3\sigma(I)$ were considered to be observed and were used in the subsequent analysis and refinement after correction for Lorentz and polarization effects. The structure was solved by the direct methods of MULTAN-80[15] and was refined by least squares with SHELX-76.[16] Hydrogen atoms were included in positions calculated from the geometry of the molecule (C–H = 1.08 Å) with a common isotropic thermal parameter which refined to a final value of $U = 0.099$ (4) Å^2. Full-matrix refinement with anisotropic thermal parameters for non-hydrogen atoms yielded a final conventional R value of 0.056, with $R_w = 0.072$. The weighting scheme adopted was

$$W = 1.00/(\sigma^2(F_o) + 0.037155(F_o)^2).$$

A final difference Fourier synthesis showed no peak >0.1 eÅ^{-3} (see supplementary material).

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Registry No. **1d**, 102342-18-7; **4d**, 2432-11-3; **11**, 17351-29-0; **12**, 102367-83-9; **13**, 102342-19-8; **14**, 93654-94-5; *cis*-2,6-diphenylcyclohexanone, 20834-02-0; *trans*-5,6-diphenylcyclohex-2-en-1-one, 70238-90-3.

Supplementary Material Available: Lists of atomic coordinates, thermal parameters, bond distances and angles, and torsion angles for **1d** (8 pages). Ordering information is given on any current masthead page.

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Reactions of Uracils. 10.[1,2] Novel Michael Adducts of Uracils and New Synthesis of Imidazo[5,1-*f*][1,2,4]triazines

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Upon treatment with ethyl propiolate (**2a**), cyanoacetylene (**2b**), and tetracyanoethylene (**5**) the 6-[(triphenylphosphoranylidene)amino]uracil **1** undergoes Michael addition to afford the 5-adducts **4a,b** and **8**. However, with diethyl azodicarboxylate Michael attack and then heterocyclic transformation occur to give the 6-(diaminomethylene)-1,2,4-triazine-1,2-dicarboxylate **11**, which can be cyclocondensed to the imidazo[5,1-*f*][1,2,4]triazine **12**.

Recently, a novel heterocyclic transformation reaction has been described involving an addition–rearrangement sequence of 6-aminouracils with acetylenedicarboxylates leading to zwitterionic amidinium–pyridinedionates and pyrrolo[3,4-*c*]pyridines.[4]

In continuation of this work we now have studied the reaction of further potential Michael addition[5] partners on 1,3-dimethyl-2,4-dioxo-6-[(triphenylphosphoranylidene)amino]pyrimidine (**1**). From these ethyl propiolate (**2a**), cyanoacetylene (**2b**),[6] and tetracyanoethylene (**5**) give only the Michael adducts **4a,b** and **7**[4,5] as the intermediary carbanion resulting from Michael attack is so basic that prototropy occurs more rapidly than nucleophilic attack at carbon 2; thus, no further transformation step[4] could be observed. From these intermediates **7** stabilizes spontaneously by evolution of HCN to give **8** (Scheme I).[14]

However, diethyl azodicarboxylate shows a behavior similar to the dialkyl acetylenedicarboxylates:[4] instead of forming a final Michael product by prototropy, the terminal basic nitrogen atom attacks the 2-carbonyl group of the uracil moiety. As a consequence, heterocyclic transformation occurs; intermediate **10** stabilizes to 6-[(*N*-methylamino)-(*N*-(triphenylphosphoranylidene)-amino)methylene]-3,5-dioxo-1,2,4-triazine-1,2-dicarboxylate **11**.

Unprotected 6-amino- and 6-hydrazinopyrimidines have been shown by Taylor and Sowinski[7] to react with diethyl azodicarboxylate in refluxing chlorobenzene at 150–160 °C to give the Michael adducts, namely, 5-(1,2-dicarbethoxyhydrazino) derivatives, in a way assumed, such as **13**.[7] However, in the present case, protective and steric effects of the iminophosphorane group in **1** disfavor an arrangement like **13**. Furthermore, the extension of the enaminocarbonyl resonance in **1** by the iminophosphorane rest and the high polarity of the solvent (MeCN)[8] stabilize

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(2) Part 10 of the series: Dihalogenotriphenylphosphoranes in Heterocyclic Synthesis. Part 9: Wamhoff, H.; Fassbender, F. J.; Hendrikx, G.; Puff, H.; Woller, P. *Chem. Ber.*, in press.

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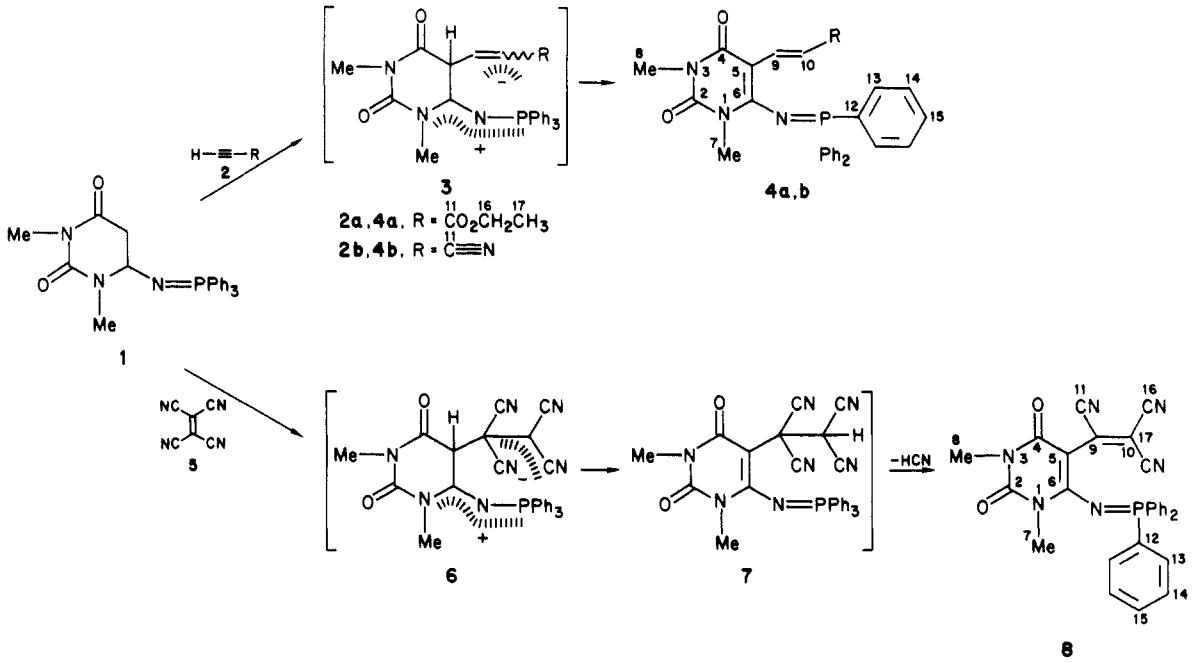
0022-3263/86/1951-2787$01.50/0

Scheme I



the transient and less basic hydrazide anion[9] of Michael adduct **10**, so that its nucleophilic attack at carbon 2 is favored. (Scheme II).

The subsequent cyclocondensation step[4] can only be performed under forcing conditions (8 h, 160 °C) and occurs in lower yield, leading to the imidazo[5,1-*f*][1,2,4]-triazine **12**. Due to a weak conjugation **12** displays in the ^{13}C NMR spectrum unusually large J_{PC} couplings (C-5, 7 Hz; C-4a, 26 Hz; C-4, no coupling) for the polarized enamine[2,10] moiety. All analytical and spectroscopic data are in best agreement with the constitutions of **4a,b**, **8**, **11**, and **12**.

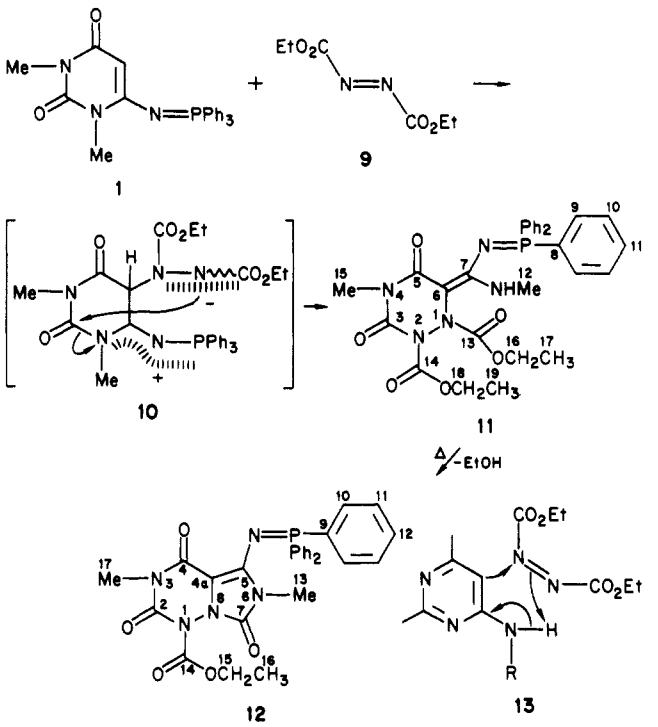
Much attention has been focused on imidazo[5,1-*f*]-[1,2,4]triazines as bronchodilators,[11] as antiviral agents,[12] and as adenosine isosteres;[13] this procedure offers a simple access to this interesting class of biologically active principles.

Experimental Section

Spectra were obtained on the following instruments: IR spectra, Perkin-Elmer 157-G; ^1H NMR spectra, Bruker WH-90; ^{13}C NMR spectra, Bruker WP-80, WH-90, and AC-200, Me_4Si as internal standard; MS, MS-30 and MS-50 of the A.E.I. (Kratos). Melting points are uncorrected. Elemental analyses were performed by Analytical Laboratory of the Institute.

1,2,3,4-Tetrahydro-1,3-dimethyl-2,4-dioxo-6-[(triphenylphosphoranylidene)amino]pyrimidine (1) was obtained according to the literature.[4]

Scheme II



Ethyl 1,2,3,4-Tetrahydro-1,3-dimethyl-2,4-dioxo-6-[(triphenylphosphoranylidene)amino]-5-pyrimidine-α-propenoate (4a). A solution of 2.07 g (5 mmol) of **1** and 0.73 g (7.5 mmol) of ethyl propiolate **2a** in 50 mL of ethanol was heated for 19 h. The solvent was then evaporated until precipitation began, which was completed by standing at 6 °C. The crude product was washed with cold ethanol and recrystallized from CH_2Cl_2/ether to give yellow crystals (1.68 g, 65.6%): mp 214 °C; IR (KBr) 1705, 1680, 1640 (CO), 1600, 1530 (C=C), 1440 (N=P) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38–7.80 (m, 15 H), 7.24 (dd, 1 H, *J* = 16 Hz, *J* = 0.5 Hz), 6.58 (d, 1 H, *J* = 16 Hz), 3.89 (q, 2 H, *J* = 7 Hz), 3.47 (s, 3 H), 3.33 (s, 3 H), 1.02 (t, 3 H, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 14.19 (C-17, q), 27.63 (C-8, q), 32.06 (C-7, q), 58.79 (C-16, t), 95.55 (C-5, d, *J* = 3 Hz), 112.32 (C-10, d), 128.34 (C-12, d, *J* = 106 Hz), 129.83 (C-14, dd, *J* = 20 Hz), 132.41 (C-13, dd, *J* = 11 Hz), 132.86 (C-15, dd, *J* = 2 Hz), 139.20 (C-9, d), 151.98 (C-2, s), 157.26 (C-6, d, *J* = 10 Hz), 162, 74 (C-4, d, *J* = 1 Hz),

(8) Refluxing of **1** and diethyl azodicarboxylate for 7 h in chlorobenzene gave no detectable reaction; **1** remained nearly unchanged.

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(14) Note added in proof. About these tricyanovinylation reactions, cf.: Fatiadi *Synthesis* **1986**, 2631.

168.58 (C-11, s); MS; m/z (relative intensity) 513 (M, 19), 183 (100). Anal. Calcd for $C_{29}H_{28}N_3O_4P$: C, 67.83; H, 5.50; N, 8.18. Found: C, 67.77; H, 5,56; N, 8.04.

1,2,3,4-Tetrahydro-1,3-dimethyl-2,4-dioxo-6-[(triphenylphosphoranylidene)amino]-5-(2-cyanoethenyl)pyrimidine (4b). To a solution of 4.16 g (10 mmol) of **1** in 10 mL of MeCN was added dropwise 0.51 g (10 mmol) of cyanoacetylene **2b** in 10 mL of MeCN. The solution was stirred for 4 days at ambient temperature. Precipitation occurred after addition of ether; recrystallization form CH_2Cl_2/ether gave yellow crystals (0.71 g, 15.2%): mp 206 °C; IR (KBr) 2225 (C≡N), 1640 (CO), 1560 (C=C), 1430 (N=P) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38–7.80 (m, 15 H), 6.87 (d, 1 H, J = 16 Hz), 6.20 (d, 1 H, J = 16 Hz), 3.44 (s, 3 H), 3.31 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 27.60 (C-8, q), 32.09 (C-7, q), 89.11 (C-10, d), 95.75 (C-5, d, J = 2 Hz), 121.06 (C-11, s), 128.20 (C-12, d, J = 107 Hz), 129.51 (C-14, dd, J = 13 Hz), 132.24 (C-13, dd, J = 10 Hz), 133.30 (C-15, dd, J = 3 Hz), 144.57 (C-9, d), 151.67 (C-2, d, J = 1 Hz), 157.14 (C-6, d, J = 10 Hz), 162.26 (C-4, d, J = 1 Hz); high-resolution MS, m/z (relative intensity) for $C_{27}H_{23}N_4O_2P$ found 466.1546 (M, 93.5), calcd 466.1554, 350 (100). Anal. Calcd for $C_{27}H_{23}N_4O_2P$: C, 69.52; H, 4.97; N, 12.01. Found: C, 69.33; H, 5.03; N, 11.83.

1,2,3,4-Tetrahydro-1,3-dimethyl-2,4-dioxo-6-[(triphenylphosphoranylidene)amino]-5-(1,2,2-tricyanoethenyl)pyrimidine (8). A solution of 4.16 g (10 mmol) of **1** and 1.28 g (10 mmol) of TCNE (**5**) in 50 mL of MeCN was stirred 10 min at ambient temperature. Then the mixture was kept at −18 °C for crystallization. After filtration, the crude product obtained was purified by column chromatography (Alox N, activity 1; 10/1 $CHCl_3$/acetone): 2.6 g (50.4%); yellow crystals, mp 222 °C; IR (KBr) 2240 (C≡N), 1710, 1645 (CO), 1520 (C=C), 1440 (N=P) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.84 (m, 15 H), 3.36 (s, 3 H), 3.29 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 28.74 (C-8, q), 32.21 (C-7, q), 90.05 (C-10, s), 95.31 (C-5, d, J = 4 Hz), 112.25, 112.64 (C-16, C-17, s, s), 114.55 114.61 (C-11, s, s, isomer configurations), 126.27 (C-12, d, J = 107 Hz), 129.86 (C-14, dd, J = 13 Hz), 132.92 (C-13, dd, J = 11 Hz), 133.84 (C-15, dd, J = 3 Hz), 134.97 (C-9, s), 151.03 (C-2, s), 158.21 (C-4, s), 158.30 (C-6, d, J = 8 Hz); MS; m/z (relative intensity) 516 (M, 100). Anal. Calcd for $C_{29}H_{21}N_6O_2P$: C, 67.44; H, 4.10; N, 16.27. Found: C, 67.90; H, 4.10; N, 16.41.

Diethyl 1,2,3,4,5,6-Hexahydro-4-methyl-3,5-dioxo-6-[(*N*-methylamino)-(*N*-(triphenylphosphoranylidene)amino)-methylene]-1,2,4-triazine-1,2-dicarboxylate (11). A suspension of 2.05 g (5 mmol) of **1** and 0.87 g (5 mmol) of diethyl azodicarboxylate (**9**) in 30 mL MeCN was heated at reflux for 6 h. After the mixture was cooled, ether was added until precipitation began. Crystallization was finalized at −18 °C; recrystallization from CH_2Cl_2/ether gave 2.7 g (91.9%) of white crystals: mp 179 °C; IR (KBr) 3335 (NH), 1770, 1745, 1700 (CO), 1625, 1590 (C=C), 1430 (N=P) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22–7.95 (m, 16 H), 3.99 (q, 2 H, J = 7 Hz), 3.61 (q, 2 H, J = 7 Hz), 3.29 (s, 3 H), 3.16 (d, 3 H, J = 10 Hz; s, after H/D exchange), 1.16 (t, 3 H, J = 7 Hz), 0.82 (t, 3 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 14.01 (C-17, q), 14.40 (C-19, q), 27.84 (C-15, q), 31.40 (C-12, q), 60.95 (C-16, t), 62.50 (C-18, t), 106.44 (C-6, d, J = 13 Hz), 128.71 (C-10, dd, J = 14 Hz), 130.04 (C-8, d, J = 100 Hz), 132.40 (C-9, dd, J = 7 Hz), 132.74 (C-11, d), 152.10 (C-13, s), 153.75 (C-14, s), 155.24 (C-3, s), 158.16 (C-7, d, J = 11 Hz), 161.74 (C-5, d, J = 9 Hz); MS, m/z (relative intensity) 589 (M, 0.5), 317 (100). Anal. Calcd for $C_{30}H_{32}N_5O_6P$: C, 61.12; H, 5.47; N, 11.88. Found: C, 60.9; H, 5.7; N, 11.6.

Ethyl 1,2,3,4,6,7-Hexahydro-3,6-dimethyl-2,4,7-trioxo-5-[(triphenylphosphoranylidene)amino]imidazo[5,1-*f*]-[1,2,4]triazine-1-carboxylate (12). **11** (3.66 g, 6.7 mmol) was heated to 160 °C in vacuo (0.2 torr) for 8 h. After the mixture was cooled, the resulting crude melted product was dissolved in CH_2Cl_2 and purified by column chromatography on Alox N (activity 1) with $CHCl_3$/acetone (10/1). The isolated material was recrystallized from CH_2Cl_2/ether: yield, 1.71 g (47%); white crystals, mp 220 °C; IR (KBr) 1810, 1780, 1735 (CO), 1580, 1555 (C=C), 1445 (N=P) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38–7.87 (m, 15 H), 4.27 (q, 2H, J = 7 Hz), 3.18 (s, 3 H), 2.67 (s, 3 H), 1.27 (t, 3 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 14.14 (C-16, q), 24.99 (C-17, q), 25.31 (C-13, q), 62.92 (C-15, t), 81.93 (C-4a, d, J = 26 Hz), 125.10 (C-9, d, J = 101 Hz), 129.20 (C-11, dd, J = 12 Hz), 133.14 (C-10, dd, J = 11 Hz), 133.55 (C-12, d), 149.67 (C-14, s), 156.43 (C-7, s), 161.90 (C-2, s), 167.79 (C-4, s), 177.50 (C-5, d, J = 7 Hz); high-resolution MS, m/z (relative intensity for $C_{28}H_{26}N_5O_5P$ found 543.1667 (M, 52), calcd 543.1666, 262 (100). Anal. Calcd for $C_{28}H_{26}N_5O_5P$: C, 61.87; H, 4.82; N, 12.88. Found: C, 61.59; H, 4.95; N, 12.66.

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Registry No. 1, 99747-54-3; **2a**, 623-47-2; **2b**, 1070-71-9; **4a**, 102587-22-4; **4b**, 102587-23-5; **5**, 670-54-2; **8**, 102587-24-6; **9**, 1972-28-7; **11**, 102587-25-7; **12**, 102587-26-8.

Synthesis of Dihydro-1,4-oxathiins by Rearrangement of 1,3-Oxathiolane Sulfoxides[1]

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A new synthesis of 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxylic acid derivatives by ring expansion of corresponding 1,3-oxathiolane 3-oxides is described. Oxidation of 2-methyl-*N*-phenyl-1,3-oxathiolane-2-acetamide (**7a**) and 2-methyl-1,3-oxathiolane-2-acetic acid methyl ester (**7b**) gave a mixture of cis and trans sulfoxides **8** and **9**, major and minor, respectively. Assignments of the cis and trans sulfoxides were based on the aromatic solvent induced ^1H NMR shifts and the regioselectivity and relative ease of purely thermal reactions of the two isomers. With PTSA as acid catalyst in C_6H_6–DMF at 50 °C both the cis and trans sulfoxides **8a** and **9a** were transformed via sulfenic acid **5a** and thiolsulfinate **10a** to a 5:4:1 mixture of β-hydroxy sulfide **2a**, dihydro-1,4-oxathiin **1a**, and acetoacetanilide **12a** in quantitative yield. This mixture was dehydrated in refluxing benzene with PTSA to obtain the desired 5,6-dihydro-2-methyl-*N*-phenyl-1,4-oxathiin-3-carboxamide (**1a**) in high yield (90%). Similar results were obtained for the cis and trans sulfoxide esters **8b** and **9b**. In the absence of an acid catalyst the cis sulfoxide **8a** at 50 °C underwent a sigmatropic rearrangement to give **5a**, followed by dimerization to **10a**. The cis sulfoxide **8b** rearranged to **10b** even below room temperature. The trans sulfoxides **9** required more drastic conditions (in DMF at 100 °C) for the conversion to isomeric dihydrooxathiin **4** via sulfenic acid **6**. The mechanism of formation of **1a** and **2a** from thiolsulfinate **10a** is also discussed.

We have been interested in the synthesis of 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxylic acid derivatives **1** since compounds of this class[2] show remarkable antifungal activity.[3] A previous synthesis, developed by Kulka

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