product which was homogeneous by TLC (10% MeOH/$CHCl_3$): mp 109–112 °C; $^1H$ NMR ($CDCl_3$) δ 1.34 (s, 9 H), 2.98 (t, 2 H, $J$ = 7 Hz), 3.54 (dt, 2 H, $J^1 = J^2$ = 7 Hz), 3.98 (t, 2 H, $J$ = 5 Hz), 4.23 (t, 2 H, $J$ = 5 Hz), 5.33 (br t, 1 H), 7.2–7.3 (m, 2 H), 7.40 (d, 1 H, $J$ = 1.5 Hz).

Anal. Calcd for $C_{16}H_{22}ClN_3O_5$: C, 56.55; H, 6.53; N, 12.37. Found: C, 56.35; H, 6.62; N, 12.35.

**2-[2-[(*tert*-Butoxycarbonyl)amino]ethyl]-1-(2-hydroxyethyl)-6-methoxybenzimidazole (8c).** This compound was prepared in the same manner as for **8a** to afford in 81% yield the desired product which was homogeneous by TLC (10% MeOH/$CHCl_3$): mp 132 °C; $^1H$ NMR ($CDCl_3$) δ 1.34 (s, 9 H), 2.84 (t, 2 H, $J$ = 6 Hz), 3.49 (dd, 2 H, $J^1 = J^2$ = 6 Hz), 3.82 (s, 3 H), 3.9–4.1 (m, 2 H), 4.1–4.3 (m, 2 H), 6.8–6.9 (m, 2 H), 7.41 (dd, 1 H, $J$ = 9, 2 Hz).

Anal. Calcd for $C_{17}H_{25}N_3O_4$: C, 60.88; H, 7.51; N, 12.53. Found: C, 60.73; H, 7.70; N, 12.34.

**2-[2-[(*tert*-Butoxycarbonyl)amino]ethyl]-6-chloro-1-[2-(*p*-toluenesulfonyloxy)ethyl]benzimidazole (9a).** A solution of **8a** (1.5 g, 4.46 mmol) and *p*-toluenesulfonyl chloride (1.0 g, 5.5 mmol) in 7.5 mL of dry pyridine was treated at 50 °C for 2 h. After cooling, the reaction mixture was partitioned between $CH_2Cl_2$ and saturated $NaHCO_3$ solution. The organic extracts were dried ($CaSO_4$) and concentrated. The remaining pyridine was removed by azeotroping with toluene under reduced pressure. The crude product, 1.6 g (70%), was obtained as a white solid which was homogeneous by TLC (silica gel, 10% MeOH/$CHCl_3$) and was used without further purification: $^1H$ NMR ($CDCl_3$) δ 1.36 (s, 9 H), 2.28 (s, 3 H), 3.01 (t, 2 H, $J$ = 6 Hz), 3.62 (br t, 2 H, $J$ = 6 Hz), 3.73 (t, 2 H, $J$ = 6 Hz), 4.34 (t, 2 H, $J$ = 6 Hz), 5.51 (br t, 1 H), 7.2–7.6 (m, 5 H), 7.55–7.8 (m, 2 H).

**2-[2-[(*tert*-Butoxycarbonyl)amino]ethyl]-1-(2-chloroethyl)-6-methoxybenzimidazole (9c).** A solution of **8c** (4.0 g, 11.9 mmol) and TsCl (2.73 g, 14.3 mmol) in 10 mL of dry pyridine was heated at 50 °C for 18 h. The reaction was then diluted with $CH_2Cl_2$ and washed with a saturated solution of $NaHCO_3$ followed by brine. After being dried ($Na_2SO_4$), the organic extracts were concentrated in vacuo. The residue was taken up in toluene and reconcentrated. This procedure was repeated to remove traces of remaining pyridine. Recrystallization of the residue from butyl chloride yielded **9c**: 2.8 g (66%); $^1H$ NMR ($CDCl_3$) δ 1.41 (s, 9 H), 3.05 (t, 2 H, $J$ = 6 Hz), 3.6–3.8 (m, 4 H), 3.88 (s, 3 H), 4.42 (t, 2 H, $J$ = 6 Hz), 5.4 (br s, 1 H), 6.79 (d, 1 H, $J$ = 2 Hz), 6.97 (dd, 1 H, $J$ = 2, 9 Hz), 7.62 (d, 1 H, $J$ = 9 Hz).

Anal. Calcd for $C_{17}H_{24}N_3ClO_3$: C, 57.70; H, 6.83; N, 11.88. Found: C, 57.31; H, 6.89; N, 11.51.

**8-Chloro-2,3,4,5-tetrahydro-1*H*-[1,4]diazepino[1,7-*a*]benzimidazole Dihydrochloride (10a).** A solution of **9a** (1.5 g, 3.0 mmol) in 20 mL of trifluoroacetic acid (TFA) was prepared at 0 °C. After the mixture was stirred at that temperature for 1 h, the TFA was removed in vacuo, and the residue was dissolved in 100 mL of 20% aqueous 2-propanol containing 3.0 g of $K_2CO_3$. This mixture was refluxed 2 h, cooled, and concentrated. The resulting solid was partitioned between $CH_2Cl_2$ and water. After the organic phase was dried ($CaSO_4$), the solvent was evaporated to afford the product as a white solid. This solid was dissolved in 15 mL of 2-propanol and acidified with ethanolic HCl. The colorless crystals which separated were filtered, washed with 2-propanol, and dried to yield 0.85 g (96%) of the dihydrochloride salt **10a**: mp 318 °C dec; $^1H$ NMR ($Me_2SO$-$d_6$/$D_2O$) δ 3.6 (m, 6 H), 4.8 (m, 2 H), 7.56 (dd, 1 H, $J$ = 8, 2 Hz), 7.79 (d, 1 H, $J$ = 8 Hz), 8.01 (d, 1 H, $J$ = 2 Hz).

Anal. Calcd for $C_{11}H_{12}ClN_3 \cdot 2HCl$: C, 44.84; H, 4.79; N, 14.26. Found: C, 44.80; H, 4.74; N, 14.16.

**9-Chloro-2,3,4,5-tetrahydro-1*H*-[1,4]diazepino[1,7-*a*]benzimidazole Dihydrochloride (10b).** Treatment of **8b** with TsCl as described for **9a** yielded the crude tosylate **9b**. This material was directly deprotected and cyclized by the procedure used to prepare **10a**, affording **10b** in 45% overall yield from **8b**: mp 290–292 °C dec; $^1H$ NMR ($Me_2SO$-$d_6$) δ 3.3–3.8 (m, 6 H), 4.8–5.0 (m, 2 H), 7.57 (dd, 1 H, $J$ = 9, 2 Hz), 7.91 (d, 1 H, $J$ = 2 Hz), 7.94 (d, 1 H, $J$ = 9 Hz).

Anal. Calcd for $C_{11}H_{12}ClN_3 \cdot 2HCl$: C, 44.84; H, 4.79; N, 14.26. Found: C, 44.88; H, 4.83; N, 14.27.

**8-Methoxy-2,3,4,5-tetrahydro-1*H*-[1,4]diazepino[1,7-*a*]benzimidazole Dihydrochloride Hemihydrate (10c).** Deprotection and cyclization of **9c** by the procedure described for the preparation of **10a** afforded **10c**: 62% yield; mp 289–293 °C dec; $^1H$ NMR ($Me_2SO$-$d_6$) δ 3.4–3.8 (m, 6 H), 3.88 (s, 3 H), 4.9 (m, 2 H), 7.15 (dd, 1 H, $J$ = 9, 2 Hz), 7.62 (d, 1 H, $J$ = 2 Hz), 7.70 (d, 1 H, $J$ = 9 Hz).

Anal. Calcd for $C_{12}H_{15}N_3O \cdot 2HCl \cdot 0.5H_2O$: C, 48.17; H, 6.06; N, 14.05. Found: C, 48.41; H, 6.00; N, 13.79.

**Acknowledgment.** We thank Ms. J. Murphy for NMR spectra and Mr. J. P. moreau for elemental analyses.

**Registry No. 2a**, 4499-07-4; **2b**, 80028-68-8; **3**, 80028-69-9; **3** chloroacetamide, 80028-70-2; **5a**, 50610-29-2; **5b**, 59320-13-7; **5c**, 78213-34-0; **6a**, 63387-85-9; **6b**, 33141-10-5; **6c**, 79858-71-2; **7a**, 78056-08-3; **7b**, 80028-71-3; **7c**, 80028-72-4; **8a**, 78056-10-7; **8b**, 80028-73-5; **8c**, 80028-74-6; **9a**, 78056-11-8; **9b**, 80028-75-7; **9c**, 80028-76-8; **10a**, 78056-12-9; **10b**, 80028-77-9; **10c**, 80028-78-0; 3-aminopropionic acid, 107-95-9; di-*tert*-butyl dicarbonate, 24424-99-5.

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## Pyrimido[4,5-*c*]pyridazines. 4. Cyclizations with α-Keto Acids

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*Received March 30, 1981*

In this report we describe the cyclization behavior of 6-(1-alkylhydrazino)isocytosines (**1**) with four α-keto acids in refluxing water. Most of our findings were unexpected in view of the information contained in earlier papers.

We reported previously[1] that reactions of 6-(1-alkylhydrazino)isocytosines (**1**) with a variety of simple α-keto esters (**2**) in refluxing water produce the highly insoluble pyrimido[4,5-*c*]pyridazine-4,5(1*H*,6*H*)-diones (**3**, Scheme I) in good yields (51–87%). With the nonalkylated analogue **1** ($R^1$ = H) and methyl pyruvate we isolated only the hydrazone **4** which appeared to be resistant to pyrimidopyridazine formation under the reaction conditions or in the presence of acidic or basic catalysts.

The failure of **4** to cyclize was not surprising in view of Pfleiderer's earlier study of the chemistry of 1,3-dimethyl-6-hydrazinouracil with simple α-keto acids and esters.[2] Reaction with methyl pyruvate in refluxing water proceeded only to the hydrazone **5a** which showed no tendency to cyclize. Furthermore, an attempted ring closure with refluxing aqueous bicarbonate effected only ester cleavage to the stable hydrazone **5b**. A similar reaction with oxomalonic acid stopped at the hydrazone stage (compound **6**), although cyclization to a pyrimido[4,5-*c*]pyridazine did occur with the corresponding diethyl ester.

In contrast with Pfleiderer's experience with the stable hydrazones **5b** and **6**, we now report that pyruvic acid and phenylglyoxylic acid react rapidly with **1a** (Scheme II) to give the known[1] pyrimido[4,5-*c*]pyridazine-4,5(1*H*,6*H*)-diones **3a** and **3b**, respectively, in isolated yields virtually identical with those from the corresponding α-keto ester cyclizations. Furthermore, unlike the ethyl ester of phenylpyruvic acid which cyclized readily (in methanol) with **1a** to give pyrimidopyridazine **3c**, phenyl- and (*p*-hydroxyphenyl)pyruvic *acids* cyclized rapidly with **1a** and

(1) Morrison, R. W.; Mallory, W. R.; Styles, V. L. *J. Org. Chem.* **1978**, *43*, 4844.
(2) Pfleiderer, W.; Ferch, H. *Justus Liebigs Ann. Chem.* **1958**, *615*, 48.

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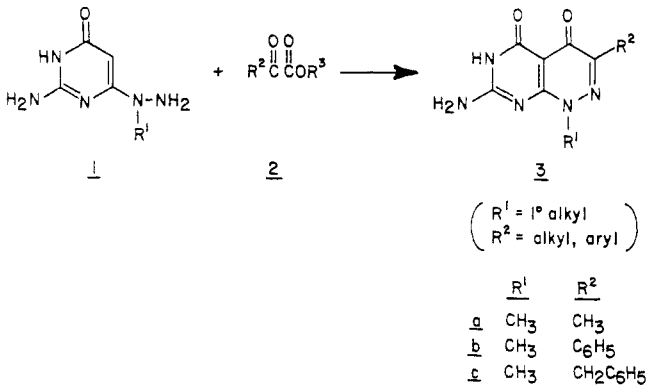
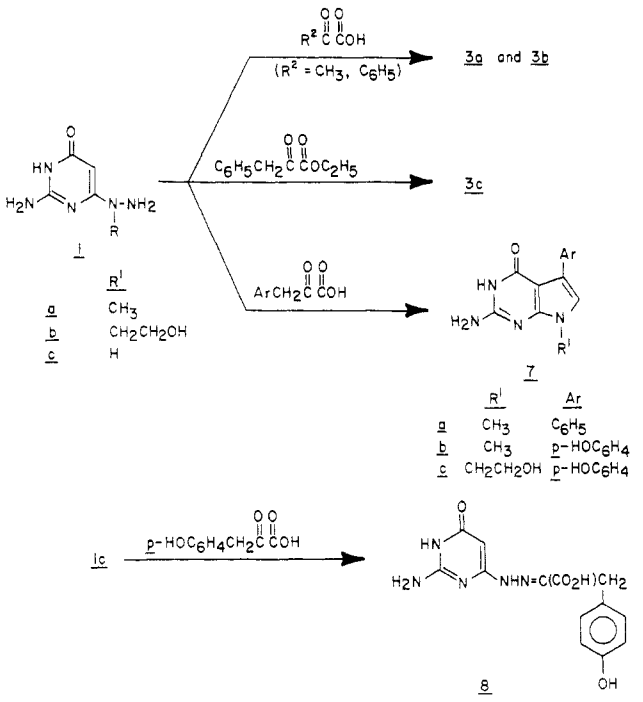
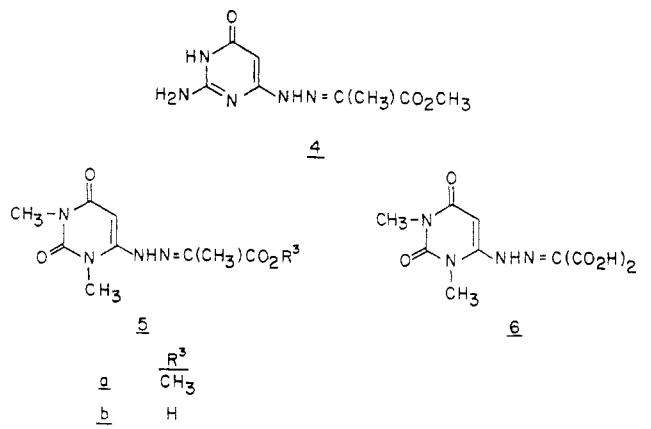
Scheme I



Scheme II



1b in refluxing water to give the novel pyrrolo[2,3-*d*]pyrimidines 7a–c in modest yields. Cyclization at the pyrimidine C-5 position was confirmed by the absence of the pyrimidine C-5 protons and the presence of the characteristically broad, low-field absorptions (ring N–H) in the NMR spectra of these products. Finally, 6-hydrazinoisocytosine (1c) formed the stable hydrazone 8 with (*p*-hydroxyphenyl)pyruvic acid in almost quantitative yield. The failure of 8 to cyclize is in agreement with the stability of the other N-nonalkylated hydrazones 4, 5b, and 6.

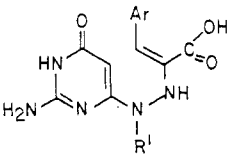


## Discussion

Although the reactions of 1 with α-keto acids in water produced complex mixtures, we consider them to be synthetically useful because the insoluble major products were usually produced in a relatively high state of purity. Examination of the mother liquor after the isolation of 3a (Scheme II) indicated a multitude of products; further refluxing of a portion of this mother liquor produced a black tar. We did not separate and characterize pure products by fractionation of the mother liquor, but we searched these fractions (by NMR, UV, and mass spectrometry) for the pyrrolopyrimidine and found no evidence for its presence at a significant level. Conversely, when the insoluble pyrimidopyridazine-4,5-diones were formed in the reactions leading to the pyrrolopyrimidnes 7, their presence was easily detected as in the case with 7a (see Experimental Section). In fact, when the reactions with phenyl- and (*p*-hydroxyphenyl)pyruvic acids were carried out in methanol (normally our solvent of choice for pyrimidopyridazine synthesis), the yields of pyrrolopyrimidines (after 24 h of reflux) were comparable with those from aqueous media. However, substantial contamination with pyrimidopyridazine (present in ca. 10% yield) occurred.

Pyrrolopyrimidines have been prepared with limited success by noncatalytic, thermally induced rearrangements of simple pyrimidinyl hydrazones and are postulated to result from a process similar to the Fischer indole synthesis.[3,4] Amarnath and Madhav have suggested that pyrimidinyl hydrazones fail to undergo the usual Fischer indolization type of reaction in acidic media because of deactivation of the pyrimidine ring for electrophilic attack due to protonation on ring nitrogen.[5] A Fischer process, or a variation thereof, could explain the formation of our pyrrolopyrimidines (7) if a decarboxylation occurred at some stage. However, the Fischer process also predicts pyrrolopyrimidine formation from pyruvic acid and 1.

Obviously, the arylpyruvic acids have special properties which cause their choice of cyclization pathway to be different from that of the simple α-keto acids. One might expect the arylpyruvic acids (because of the possibility of conjugation with their aromatic rings) to form more stable ene–hydrazine intermediates 9 (even if only as minor



components in equilibrium mixtures with the tautomeric hydrazones). These species (9) would be requisite for Fischer-type [3,3] sigmatropic rearrangements or Michael additions leading eventually to pyrrolopyrimidines. The cyclizations to pyrrolopyrimidines were so rapid, however, that we did not isolate an intermediate product. The NMR spectrum for the one arylpyruvic acid hydrazone isolated, 8, suggests that no detectable amount of ene–hydrazine is present when in $Me_2SO$-$d_6$ solution (δ 3.62, s, $CH_2Ar$). Since hydrazone 8 did not cyclize (most likely because its hydrazino group was not alkylated), it may not represent a relevant comparison. Finally, we have no explanation for the preferred cyclization of 1a with phe-

(3) Senda, S.; Hirota, K. *Chem. Pharm. Bull.* **1974**, *22*, 1459.
(4) Duffy, T.; Wibberley, D. G. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1921.
(5) Amarnath, V.; Madhav, R. *Synthesis* **1974**, 848.

nylpyruvic ester to give pyrimidopyridazine **3c** and with phenylpyruvic acid to give pyrrolopyrimidine **7a**.

## Conclusions

We conclude that the simple $\alpha$-keto acids (pyruvic and phenylglyoxylic) are as useful as their esters for the preparation of pyrimido[4,5-*c*]pyridazine-4,5(1*H*,6*H*)-diones from 6-(1-*alkyl*hydrazino)isocytosines (**1**). Phenyl- and (*p*-hydroxyphenyl)pyruvic acids cyclize with **1** in refluxing water to give 5-aryl-7-alkylpyrrolo[2,3-*d*]pyrimidines in modest, but synthetically useful, yields. However, alkylation of the hydrazino substituent of **1** appears to be necessary for either type of cyclization.

## Experimental Section

Melting points were run on a Thomas-Hoover capillary melting point apparatus. NMR spectra were determined with Varian XL-100 of CFT-20 spectrometers with tetramethylsilane as the internal standard; Fourier transform was utilized in cases of poor solubility. The nuclear Overhauser effect (NOE) is expressed as $f_I(S)$ which is the fractional enhancement of nucleus I due to saturation of nucleus S. Low-resolution mass spectra were obtained with a Varian MAT CH5 DF mass spectrometer; an accurate mass was determined by peak matching at 10000 resolution, 10% valley definition. Microanalyses were performed by Atlantic Microlab, Inc. All C, H, and N analyses not reported here were acceptable (±0.3%) and can be found along with other physical data in the supplementary material. Pyruvic acid was obtained from Matheson Coleman & Bell Manufacturing Chemists. (*p*-Hydroxyphenyl)pyruvic and phenylglyoxylic acids were obtained from Aldrich Chemical Co. Phenylpyruvic acid was obtained from Pfaltz and Bauer.

**2-Amino-5-(4-hydroxyphenyl)-7-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4(3*H*)-one (7b).** To a solution of 0.82 g (5.0 mmol) of **1a** (as the hemihydrate)[1] in 75 mL of water stirred at reflux was added 1.08 g (6.0 mmol, 98% purity) of (*p*-hydroxyphenyl)pyruvic acid. Under nitrogen, reflux was continued for 2 h, and the resulting mixture was allowed to cool to ambient temperature. The yellow solid was collected by filtration, washed with water, and dried under vacuum at 70 °C; yield 0.35 g. Recrystallization from methanol under a nitrogen atmosphere afforded 0.32 g (22%) of **7b** as yellow crystals: mp >300 °C;[6] $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 3.51 (s, 3 H), 6.19 (br s, 2 H), 6.68 (d, $J$ = 8.7 Hz, 2 H), 6.88 (s, 1 H), 7.71 (d, $J$ = 8.7 Hz, 2 H), 9.15 (s, 1 H), 10.23 (br s, 1 H), and methanol, 3.17 (d, J = 5.3 Hz, 3 H), 4.07 (q, 1 H); NOE $f_{6.88}$(3.51) = 28%; $^{13}$C NMR ($Me_2SO$-$d_6$) $\delta$ 158.9 (C-4), 155.4 (C-7a), 152.2 (C-2), 151.4 (C-4′), 128.5 (d, C-2′ and C-6′), 125.5 (C-1′), 119.1 (C-5), 117.8 (d, $^1J_{CH}$ = 185.6 Hz, C-6), 114.6 (d, $^1J_{CH}$ = 158 Hz, C-3′ and C-5′), 97.0 (d, $^3J_{CH}$ = 5.1 Hz, C-4a), 30.4 (q, $^1J_{CH}$ = 139 Hz, $NCH_3$);[7] UV ($CH_3OH$) $\lambda_{max}$ 250 nm ($\epsilon$ 24400), 281 (11900), 299 (13200); mass spectrum (260 °C), *m/e* (relative intensity) 256 (M, 100), accurate mass *m/e* 256.0969 ($C_{13}H_{12}N_4O_2$). Anal. Calcd for $C_{13}H_{12}N_4O_2$·$CH_3OH$: C, 58.32; H, 5.60; N, 19.43. Found: C, 58.26; H, 5.61; N, 19.44.

Similarly prepared were **3a,b** and **7a,c**. The starting isocytosine, starting $\alpha$-keto acid, and reaction time are given in brackets, followed by the yield and melting point.

**7-Amino-1,3-dimethylpyrimido[4,5-*c*]pyridazine-4,5-(1*H*,6*H*)-dione (3a)**[1] [**1a**, pyruvic acid, 1 h]: 48%; mp >300 °C. Anal. $C_8H_9N_5O_2$. Physical parameters were found to be identical with those of the authentic sample.

**7-Amino-1-methyl-3-phenylpyrimido[4,5-*c*]pyridazine-4,5(1*H*,6*H*)-dione (3b)**[1] [**1a**, phenylglyoxylic acid (50% molar excess), 1 h]: 56%; mp >300 °C. Anal. ($C_{13}H_{11}N_5O_2$·$0.5H_2O$). Identified as **3b** by NMR, UV, and TLC comparisons with the original sample.

**2-Amino-7-methyl-5-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-4(3*H*)-one (7a)**[8] [**1a**, phenylpyruvic acid, 1 h]: 22% (after recrystallization from methanol); mp > 300 °C. Anal. $C_{13}H_{12}N_4O$·$0.25H_2O$.

**2-Amino-7-(2-hydroxyethyl)-5-(4-hydroxyphenyl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-4(3*H*)-one (7c)** [**1b**,[1] (*p*-hydroxyphenyl)pyruvic acid, 1.5 h]: 27%; mp >280 °C dec. Anal. $C_{14}H_{14}N_4O_3$·$0.5H_2O$.

**2-[(2-Amino-1,6-dihydro-6-oxo-4-pyrimidinyl)-hydrazono]-3-(4-hydroxyphenyl)propionic acid (8)** [**1c**,[1] (*p*-hydroxyphenyl)pyruvic acid, 5 h]: 96%; mp 283-284 °C dec. Anal. $C_{13}H_{13}N_5O_4$.

**Acknowledgment.** We thank Dr. B. S. Hurlbert, Mr. R. Crouch, and Mr. A. Ragouzeos for NMR spectra, Dr. D. A. Brent, Mr. R. L. Johnson, and Mr. Bernd Soltman for mass spectral data, and Ms. S. Wrenn for UV studies.

**Registry No. 1a**, 67873-21-6; **1b**, 67873-23-8; **1c**, 6298-85-7; **2** ($R^2$ = *p*-$HOC_6H_4CH_2$; $R^3$ = H), 156-39-8; **2** ($R^2$ = Me; $R^3$ = H), 127-17-3; **2** ($R^2$ = Ph; $R^3$ = H), 611-73-4; **3a**, 67873-29-4; **3b**, 67873-42-1; **7a**, 80042-18-8; **7b**, 80042-19-9; **7c**, 80042-20-2; **8**, 80081-74-9.

**Supplementary Material Available:** Full data available include the following: Microanalyses for compounds **3a,b,7a,c**, and **8**, NMR and UV data on compounds **7a,c** and **8**, and mass spectral data on compound **7a** (2 pages). Ordering information is given on any current masthead page.

(6) Turned blue above 150 °C but did not melt.

(7) These data correlate well with $^{13}$C NMR data for close analogues reported by: Secrist, J. A., III; Liu, P. S. *J. Org. Chem.* **1978**, *43*, 3937.

(8) The crude product was contaminated with a small amount of 7-amino-3-benzyl-1-methylpyrimido[4,5-*c*]pyridazine-4,5(1*H*,6*H*)-dione,[1] isolated in 2% yield during the recrystallization.

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# Homogeneous, Palladium(0)-Catalyzed Exchange Deprotection of Allylic Esters, Carbonates, and Carbamates[1]

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*Received October 22, 1981*

Soluble palladium complexes are finding increased use in synthesis,[2] and the value of $\pi$-allyl complexes in particular has been demonstrated in an elegant series of investigations by Trost.[3] Here, we describe a process for cleavage of the (allyloxy)carbonyl function using catalytic $\pi$-allyl activation,[4] designed initially for carboxylate unmasking in $\beta$-lactam derivatives and generally applicable to all types of *N*- or *O*-[(allyloxy)carbonyl] structures.

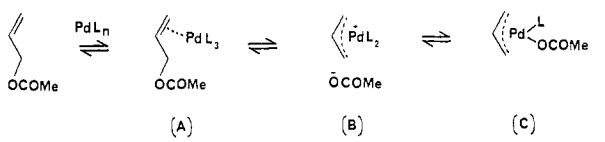
The (allyloxy)carbonyl function, originally introduced as a hydrogenolyzable N-blocking group,[5] is subject to C–O

(1) The process described herein is the subject of European Patent Office Application EP 13-663.

(2) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615-2649.

(3) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385-393.

(4) Activation involves a series of equilibria:




In the case of allylic C–C bond formation with soft nucleophiles, the cationic complex B is involved (ref 3, p 387), whereas for carboxylate nucleophiles, transfer via coordination to the metal as in C has been implicated: Backvall, J. E.; Nordberg, R. E.; Bjorkmanan, E. E.; Moberg, C. *J. Chem. Soc., Chem. Commun.* **1980**, 943-944. In support of this latter observation, we have found that, whereas a number of other phosphine–palladium combinations are effective exchange catalysts [e.g., $Pd(OAc)_2$–$PPh_3$, $Pd(OAc)_2$–$(EtO)_3P$], the presence of strongly chelating phosphine [$Pd(OAc)_2$–$Ph_2PCH_2CH_2PPh_2$] retards the process, presumably by preventing effective complexation of carboxylate ligands onto the metal center.

(5) Stevens, C. M.; Watanabe, R. *J. Am. Chem. Soc.* **1950**, *72*, 725-727.

0022-3263/82/1947-0587$01.25/0 © 1982 American Chemical Society