nism in the hydrolysis of a phosphacyl[8] derivative devoid of α-protons.

Experimental Section

General. All starting reagents and solvents were purified and/or distilled before use. Buffer materials were analytical reagent grade. Water was double distilled and preboiled to free it from dissolved gases. Dioxan was purified by passage of the analytical grade material through an activated alumina column.

***N,N*-Diethyl-*P*-(3,5-dimethyl-4-hydroxyphenyl)-phosphonamidic Chloride (1).** A solution of 2,6-dimethyl-4-bromophenol[12] (4.2 g, 20 mmol) in dry ether (25 mL) was treated with *n*-butyllithium (25 mL, 1.6 M solution in hexane, 40 mmol) at 0 °C under nitrogen. The resultant cloudy solution was stirred at room temperature for 18 h, again cooled at 0 °C, and treated with *N,N*-diethylphosphoramidic dichloride[13] (3.8 g, 20 mmol) dissolved in dry ether (5 mL). The reaction mixture was allowed to warm to room temperature; after 24 h aqueous ammonium chloride (50 mL, saturated) was added, and the separated organic layer was washed sequentially with aqueous HCl (4%, 25 mL) and water (25 mL). The organic layer was dried over sodium sulfate and filtered, and the solvent was removed under reduced pressure. Column chromatography (E. Merck silica gel 60, 1:1 methylene chloride–ethyl acetate) of the resulting yellow oil allowed isolation of 1.5 g (28% yield) of the chloride as a pale yellow liquid. A small portion of this liquid was further chromatographed on a preparative TLC plate (E. Merck silica gel 60), affording the pure product: ^{1}H NMR ($CDCl_3$, TMS) δ 7.44 (d, J_{HP} = 14.9 Hz, 2 h, ArH), 3.15 (m, 4 H, NCH_2CH_3), 2.25 (s, 6 H, $ArCH_3$), 1.12 (t, J = 7.1 Hz, 6 H, NCH_2CH_3). The identity of the product was also confirmed by converting it, through standard methods, into **2',4'-dinitrophenyl *N,N*-diethyl-*P*-(3,5-dimethyl-4-hydroxyphenyl)phosphonamidate,** which had mp 133–4 °C (petroleum ether). Anal. Calcd for $C_{18}H_{22}N_3O_7P$: C, 51.1; H, 5.2; N, 9.9. Found: C, 51.5; H, 5.3; N, 9.8.

***N,N*-Diethyl-*P*-(3,5-dimethyl-4-methoxyphenyl)-phosphonamidic Chloride (2).** This compound was obtained by allowing the chloride **1** to react, for 48 h at room temperature in dry ether, with diazomethane (generated with the aid of the Aldrich Diazald Kit). The resultant yellow solution was evaporated under reduced pressure, affording a light yellow liquid. Preparative TLC (E. Merck silica gel 60, 1:1 methylene chloride–ethyl acetate) provided the pure product: ^{1}H NMR ($CDCl_3$, TMS) δ 7.53 (d, J_{HP} = 15 Hz, 2 H, Ar*H*), 3.75 (s, 3 H, OCH_3), 3.16 (m, 4 H, NCH_2CH_3), 2.32 (s, 6 H, $ArCH_3$), 1.13 (t, J = 7.1 Hz, 6 H, NCH_2CH_3). Again, the identity of the product was assessed by conversion into **2',4'-dinitrophenyl *N,N*-diethyl-*P*-(3,5-dimethyl-4-methoxyphenyl)phosphonamidate,** mp 124–5 °C (petroleum ether). Anal. Calcd for $C_{19}H_{24}N_3O_7P$: C, 52.2; H, 5.5; N, 9.6. Found: C, 52.0; H, 5.6; N, 9.5.

Products Analysis. (a) Alkaline Hydrolysis. The NMR spectra of both the chlorides **1** and **2** (15 mg) in a 1:1 acetone-d_6/deuterium oxide mixture (0.5 mL) were recorded, and then these solutions were made alkaline by adding few microliters of NaOD ca. 14 M in D_2O, and several spectra of the resulting solutions were taken at different times. **(b) Acidic Hydrolysis.** To fresh solutions of the chlorides in the deuterated mixture was added a few microliters of DCl 37% in D_2O, and again several NMR spectra were recorded at different times.

Kinetics. All kinetic measurements were done spectrophotometrically by recording the decrease in absorbance at either 277 or 236 nm due to the disappearance, respectively, of the chlorides **1** and **2**. In a typical run, the buffered solution (2.5 mL) was allowed to equilibrate to the required temperature in a 1-cm path length quartz cell placed in the thermostatted cell holder of the spectrophotometer. The reaction was initiated by adding an aliquot (10 μL) of the stock solution of the chloride (ca. 10^{-2} M) in dioxane. Reactions were usually followed over about 7 half-lives. The pH of the reactant buffers were measured before and after the reaction at the appropriate temperature. No buffer concentration effects were observed on the rates of hydrolysis of chloride **1** in the range of buffer concentrations employed (0.01–0.1 M). In the case of chloride **2** small effects were observed, and the rate constants at zero buffer concentration were obtained by extrapolation. The ionic strength was maintained at 1 M with potassium chloride. The pseudo-first-order rate constants were calculated on an Apple IIe PC with a program written by one of us (S.T.). The activation parameters were determined measuring the rates of hydrolysis at three temperatures (see Table I).

Registry No. 1, 129835-85-4; 2, 129835-86-5; 2,6-dimethyl-4-bromophenol, 2374-05-2; *N,N*-diethylphosphonamidic acid, 1498-54-0; 2',4'-dinitrophenyl *N,N*-diethyl-*p*-(3,5-dimethyl-4-hydroxyphenyl)phosphonamidate, 129835-87-6; 2',4'-dinitrophenyl *N,N*-diethyl-*p*-(3,5-dimethyl-4-methoxyphenyl)phosphonamidate, 129835-87-6.

Supplementary Material Available: Two tables reporting observed rate constants for the hydrolysis of the substrates (2 pages). Ordering information is given on any current masthead page.

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Ring Contraction of 1,2,4-Triazepino[2,3-*a*]benzimidazol-4-ones. New Fused β-Lactams

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Received March 27, 1990

Isolation of uncommon fused tetracyclic β-lactams **2** strongly supports a previously unconfirmed ionic mechanism for the ring contraction of nitrogen-bridged azolo-1,2,4-triazepin-3-ones in acetic anhydride. Procedures for the synthesis in good yields of substituted-pyrazolo[1,5-*a*]benzimidazoles from the corresponding [1,2,4]triazepino[2,3-*a*]benzimidazoles are reported.

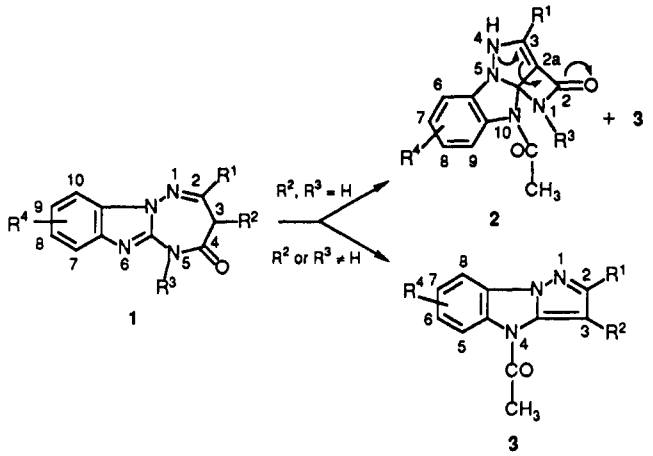
Introduction

Gehlen and Drohla reported for the first time in 1970 the reaction between nitrogen-bridged triazepinones derived from 1,2-diamino-1,3,4-triazoles and ethyl acetoacetate in acetic anhydride solution. Two alternative structures, imidazo[2,1-*c*]-*s*-triazole or imidazo[1,2-*b*]-*s*-triazole, were proposed for the reaction products.[1] Four years later, Claramunt et al. firmly established that those ring-contraction products were pyrazolo[3,2-*c*]-*s*-triazoles and were, consequently, able to give the correct structure

(1) Gehlen, H.; Drohla, R. *Arch. Pharm.* **1970**, *303*, 709.

0022-3263/91/1956-0074$02.50/0

Table I. Ring Contraction of [1,2,4]Triazepino[2,3-*a*]benzimidazol-4-ones with Acetic Anhydride



starting compound		isolated and recrystallized products (% yield)	
1a[5]	$R^1 = CH_3$, $R^2 = R^3 = R^4 = H$	**2a** (31)	**3a** (18)
1b[5]	$R^1 = CH_3$, $R^2 = R^3 = H$, R^4 = 8,9-dimethyl	**2b** (9)	**3b** (37)
1c	R^1 = propyl, $R^2 = R^3 = R^4 = H$	**2c** (10)	**3c** (traces)
1d	R^1 = propyl, $R^2 = R^3 = H$, R^4 = 8,9-dimethyl	**2d** (5)	**3d** (12)
1e	$R^1 = F_3C$, $R^2 = R^3 = R^4 = H$		**3e** (98)
1f	$R^1 = F_3C$, $R^2 = R^3 = H$, R^4 = 8,9-dimethyl		**3f** (55)
1g	R^1 = Ph, $R^2 = R^3 = R^4 = H$		**3g** (60)
1h[5]	$R^1,R^2 = (CH_2)_4$, $R^3 = R^4 = H$		**3h** (100)
1i	$R^1,R^2 = (CH_2)_4$, $R^3 = H$, R^4 = 8,9-dimethyl		**3i** (81)
1j[5]	$R^1 = R^2 = CH_3$, $R^3 = R^4 = H$		**4j** (98)
1k	$R^1 = R^2 = CH_3$, $R^3 = H$, R^4 = 8,9-dimethyl		**4k** (84)
1l	$R^1 = R^3 = CH_3$, $R^2 = R^4 = H$		**3a** (98)

for the starting triazepinones.[2,3] An ionic mechanism involving a fused β-lactam intermediate was suggested to explain the loss of cyanic acid,[4] but a definitive confirmation has not been reported so far.

The accessibility of triazepinones derived from condensation of 1,2-diaminobenzimidazoles and β-oxo esters prompted us to extend the number of the previously described derivatives[5] in order to study the above-mentioned reaction.

Results and Discussion

Treatment of triazepinones **1e–l** (Table I) with acetic anhydride gave acetylpyrazolo[1,5-*a*]benzimidazoles **3e–4k** in almost quantitative yields. Remarkably, in the case of triazepinones **1a–d** we succeeded in the isolation of β-lactams (±)-**2a–d**.

Structure assignment of β-lactams **2** was based on spectroscopic evidence (see Experimental Section) as well as on their alkaline hydrolysis to carboxamides **5**. We compare in Figure 1 the assigned ^{13}C NMR chemical shift values of 2-methyl-3*H*-[1,2,4]triazepino[2,3-*a*]benzimidazol-4-one (**1a**)[5] with those of its corresponding ring-contraction product 3-methyl-10-acetyl-4*H*-azeto-

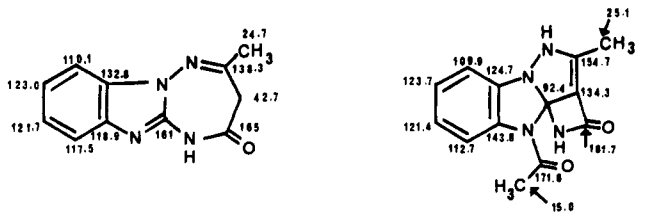
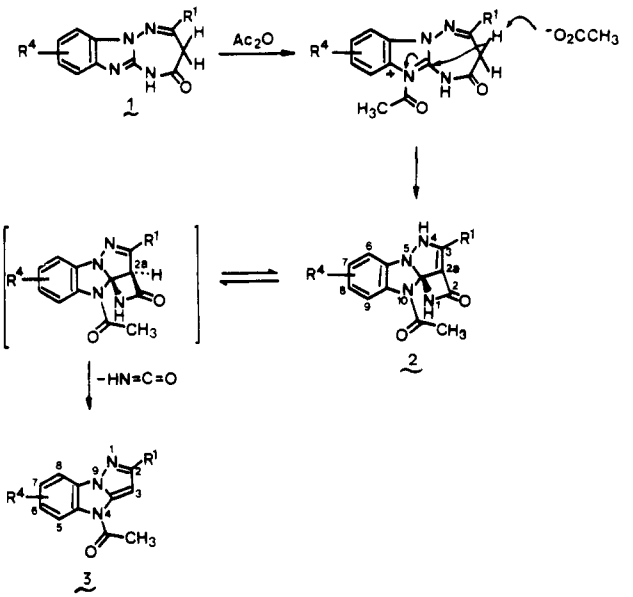


Figure 1.

Scheme I



[3′,2′:4,5]pyrazolo-[1,5-*a*]benzimidazol-2-one (**2a**). Although to our knowledge there are no literature references about this type of compound, the ^{13}C NMR signals are consistent with the proposed structure. The main observed changes are the dissapearance of the C-3 signal of **1a** at δ = 42.7 and the appearance of a new C_{sp^3} resonance at 92.4. This signal is assigned to the carbon atom C-10a of **2a**.

Two C=O stretching values were found in the infrared spectra of compounds **2**. The higher frequency, at about 1700 cm^{-1}, must correspond to the acetyl carbonyl group (see compounds **3**). The extremely low frequency value of the other band, at about 1660 cm^{-1}, is in agreement with the proposed α,β-unsaturated β-lactam carbonyl group.

From the fact that only β-lactams derived from 3-unsubstituted triazepinones (**1**, R^2 = H) have been isolated, it can be inferred that the conjugated 4*H* tautomer of **2** is more stable than its unconjugated 2a*H* tautomer (Scheme I). Electron delocalization of the unshared electron pair on the N-4 nitrogen atom into the α,β-unsaturated carbonyl system in compounds **2** provides sufficient stabilization of the lactam structures to allow their isolation. The unstable nonconjugated 2a*H* tautomers are therefore the most likely precursors of compounds **3** and **4** by ejection of cyanic acid. Although we do not have experimental evidence, acetamide (or $R^3NHCOCH_3$) and CO_2 would be the final side products.[6]

Electronic effects of the substituents R^1 must play a role in the equilibrium between both β-lactam tautomers (2a*H* ⇄ 4*H*), since the only isolated β-lactams were those derived from triazepinones bearing an electron-releasing substituent at C-2.

In the case of the 5-methyl derivative **1l**, obtained by reaction of **1a** with diazomethane, the loss of methyl iso-

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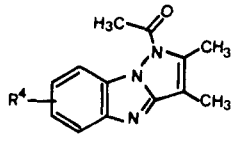
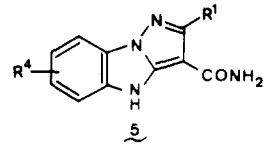
cyanate from the corresponding more crowded 1-methyl-β-lactam must take place to give **3a**.

Compounds **3** and **4** are 4-acetyl and 1-acetyl derivatives of N-unsubstituted pyrazolo[1,5-*a*]benzimidazole and can be considered as two fixed models. Structures **3** are in accordance to the established greater stability of the N4-*H* tautomer.[7-9] The structures **4**, which have been deduced by considering the observed anisotropic effect of the acetyl group on the H-8 aromatic proton,[10] have been only observed in the 3-methyl derivatives (**4j** and **4k**). The steric effects between the R^2 (Me) and N4-acetyl groups in the unisolated compounds **3j** and **3k** must play a key role as the driving force for transacylation to the less conjugated N1-acetyl isomers **4j** and **4k**.

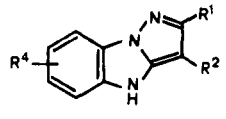
Both type of compounds were deacetylated to **6** by acid hydrolysis. It should be mentioned that compounds **3a** and **6a**, previously prepared by other routes, have been extensively studied in relation to the chemical behavior of [5,5]heteroaromatic systems.[7-10]



4



5



6

Experimental Section

Melting points were uncorrected and determined on a Büchi capillary melting point apparatus. IR spectra were recorded on a Pelkin-Elmer 577 spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on Perkin-Elmer R24-B (60 MHz), Brucker WM 200-SY (200 MHz, 50 MHz), and Varian VXR-300 (300 MHz) spectrometers. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane. All compounds gave microanalysis according to their structures. Chromatographic purifications were carried out through columns either at natural pressure using silica gel 70–230 mesh or by the Still method.[11]

[1,2,4]Triazepino[2,3-*a*]benzimidazol-4-ones were prepared by condensation of 1,2-diaminobenzimidazole and the corresponding β-oxo ester following ref 5.

2-Propyl-3*H*-[1,2,4]triazepino[2,3-*a*]benzimidazol-4-one (1c): pink crystals, 30% yield; mp 259–260 °C (methanol); ^1H NMR (300 MHz, DMSO-d_6) δ 7.55–7.46 (m, 2 H, H-7, H-10), 7.29–7.20 (m, 2 H, H-8, H-9), 3.62 (s, 2 H, H-3), 2.62 (t, J = 7.0 Hz, 2 H, CH_2), 1.68 (m, 2 H, CH_2), 0.94 (t, J = 7.0 Hz, 3 H, CH_3); IR (KBr) 3000–2500, 1680, 1620, 1580 cm^{-1}. Anal. Calcd for $C_{13}H_{14}N_4O$: C, 64.44; H, 5,82; N, 23.12. Found: C, 64.46; H, 5.98; N, 23.42.

2-Propyl-8,9-dimethyl-3*H*-[1,2,4]triazepino[2,3-*a*]benzimidazol-4-one (1d): pink crystals, 25% yield; mp 295–296 °C dec (ethanol); ^1H NMR (300 MHz, DMSO-d_6) δ 7.29 (s, 1 H, Ar-H), 7.25 (s, 1 H, Ar-H), 3.48 (s, 2 H, H-3), 2.60 (t, J = 7.0 Hz, 2 H, CH_2), 2.33 (s, 3 H, Ar-Me), 2.31 (s, 3 H, Ar-Me), 1.69 (m, 2 H, CH_2), 0.95 (t, J = 7.0 Hz, 3 H, CH_3); IR (KBr) 3200–2200, 1700, 1625, 1595 cm^{-1}. Anal. Calcd for $C_{15}H_{18}N_4O$: C, 66.63; H, 6.71; N, 20.72. Found: C, 66.34; H, 6.88; N, 20.99.

2-(Trifluoromethyl)-3*H*-[1,2,4]triazepino[2,3-*a*]benzimidazol-4-one (1e): white crystals, 20% yield, mp 293–294 °C dec (ethanol); ^1H NMR (200 MHz, DMSO-d_6) δ 12.16 (ws, 1 H, H-5), 7.58–7.44 (m, 2 H, H-7, H-10), 7.38–7.26 (m, 2 H, H-8, H-9), 3.97 (s, 2 H, H-3); IR (KBr) 3000–2500, 1700, 1650, 1590 cm^{-1}. Anal. Calcd for $C_{11}H_7F_3N_4O$: C, 49.25; H, 2.63; N, 20.89. Found: C, 49.10; H, 2.81; N, 20.70.

2-(Trifluoromethyl)-8,9-dimethyl-3*H*-[1,2,4]triazepino[2,3-*a*]benzimidazol-4-one (1f): white crystals, 13% yield, mp > 300 °C (dimethylformamide); ^1H NMR (60 MHz, F_3CCO_2H) δ 7.60 (s, 1 H, Ar-H), 7.55 (s, 1 H, Ar-H), 4.20 (s, 2 H, H-3), 2.50 (s, 6 H, Ar-Me); IR (KBr) 3000–2500, 1690, 1655, 1590 cm^{-1}. Anal. Calcd for $C_{13}H_{11}F_3N_4O$. C, 52.70; H, 3.74; N, 18.91. Found: C, 52.93; H, 3.93; N, 19.10.

2-Phenyl-3*H*-[1,2,4]triazepino[2,3-*a*]benzimidazol-4-one (1g): white crystals, 7% yield, mp 296–297 °C dec (dimethylformamide); ^1H NMR (300 MHz, DMSO-d_6) δ 11.92 (ws, 1 H, H-5), 8.15–8.05 (m, 2 H, H-2′, H-6′), 7.65–7.55 (m, 5 H, Ar-H), 7.35–7.25 (m, 2 H, H-8,9) 4.10 (s, 2 H, H-3); IR (KBr) 3600–2200, 1685, 1625, 1585 cm^{-1}. Anal. Calcd for $C_{16}H_{12}N_4O$; C, 69.55; H, 4.37; N, 20.28. Found: C, 69.45; H, 4.64; N, 20.40.

2,3-Tetramethylene-8,9-dimethyl-3*H*-[1,2,4]triazepino[2,3-*a*]benzimidazol-4-one (1i): white crystals, 33% yield, mp > 300 °C (dimethylformamide); ^1H NMR (300 MHz, DMSO-d_6) δ 8.17 (s, 1 H, H-10), 7.25 (s, 1 H, H-7), 2.62 (m, 2 H, CH_2), 2.48 (overlapped m, CH_2), 2.34 (s, 6 H, Ar-Me), 1.73 (m, 4 H, CH_2CH_2); IR (KBr) 3300–2300, 1675, 1575 cm^{-1}. Anal. Calcd for $C_{16}H_{18}N_4O$: C, 68.06; H, 6.42; N, 19.84. Found: C, 68.30; H, 6.42; N, 19.66.

(±)-2,3,8,9-Tetramethyl-3*H*-[1,2,4]triazepino[2,3-*a*]benzimidazol-4-one (1k): white crystals, 55% yield, mp 287–288 °C dec (ethanol); ^1H NMR (60 MHz, DMSO-d_6) δ 7.35 (s, 2 H, Ar-H), 3.60 (q, J = 7.0 Hz, 1 H, H-3), 2.30 (s, 6 H, Ar-Me), 2.20 (s, 3 H, Me-2), 1.35 (d, J = 7.0 Hz, 3 H, Me-3); IR (KBr) 3000–2280, 1685, 1590 cm^{-1}. Anal. Calcd for $C_{14}H_{16}N_4O$: C, 65.60; H, 6.29; N, 21.86. Found: C, 65.82; H, 6.47; N, 22.06.

2,5-Dimethyl-3*H*-[1,2,4]triazepino[2,3-*a*]benzimidazol-4-one (1l). To a solution of **1a** (0.5 g, 2.33 mmol) in methanol (150 mL) at 5 °C was added a solution of diazomethane (1.30 g, 3.09 mmol) in ether (50 mL) dropwise. After 24 h, the solvent was removed and the solid residue was recrystallized. Pink crystals, 38% yield, mp 126–127 °C (ethanol–water); ^1H NMR (60 MHz, DMSO-d_6) δ 7.70–7.10 (m, 4 H, Ar-H), 3.68 (s, 2 H, H-3), 3.43 (s, 3 H, Me-5), 2.35 (s, 3 H, Me-2); IR (KBr) 1705, 1640, 1620, 1600 cm^{-1}. Anal. Calcd for $C_{12}H_{12}N_4O$: C, 63.14; H, 5.29; N, 24.54. Found: C, 62.92; H, 5.29; N, 24.26.

Ring-Contraction Reactions. A suspension of **1** (5 mmol) in an excess of acetic anhydride was refluxed for 1 h, and the reaction mixture was then evaporated in vacuo. The crude products were separated by column chromatography on silica gel, using ethyl acetate as eluent, and recrystallized in the appropriate solvent.

(±)-3-Methyl-10-acetyl-4*H*,10*H*-azeto[3′,2′:4,5]pyrazolo[1,5-*a*]benzimidazol-2-one (2a): white crystals, mp > 300 °C (methanol); ^1H NMR (200 MHz, DMSO-d_6) δ 12.65 (s, 1 H, H-4), 10.05 (s, 1 H, H-1), 7.76 (dd, J = 7.0, 1.3 Hz, 1 H, H-9), 7.55 (dd, J = 7.0, 1.3 Hz, 1 H, H-6), 7.38–7.30 (m, 2 H, H-7, H-8), 2.51 (s, 3 H, $COCH_3$), 2.30 (s, 3 H, Me-3); ^{13}C NMR (50 MHz, DMSO-d_6) δ 171.6 ($COCH_3$), 161.7 (C-2), 154.7 (C-3), 143.8 (C-9a), 134.3 (C-2a), 124.7 (C-5a), 123.7 (C-7), 121.4 (C-8), 112.7 (C-9), 109.9 (C-6), 92.4 (C-10a), 25.1 (Me-3), 15.0 ($COCH_3$); IR (KBr) 1700, 1655, 1600 cm^{-1}. Anal. Calcd for $C_{13}H_{12}N_4O_2$: C, 60.92; H, 4.72; N, 21.86. Found: C, 60.75; H, 4.49; N, 21.48.

(±)-3,7,8-Trimethyl-10-acetyl-4*H*,10*H*-azeto[3′,2′:4,5]pyrazolo[1,5-*a*]benzimidazol-2-one (2b): white crystals, mp > 300 °C (ethanol); ^1H NMR (300 MHz, DMSO-d_6) δ 12.12 (s, 1 H, H-4), 9.95 (s, 1 H, H-1), 7.55 (s, 1 H, H-9), 7.30 (s, 1 H, H-6), 2.50 (overlapped s, $COCH_3$), 2.34 (s, 6 H, Ar-Me), 2.30 (s, 3 H, Me-3); ^{13}C NMR (50 MHz, DMSO-d_6) δ 171.7 ($COCH_3$), 161.7 (C-2), 154.3 (C-3), 143.6 (C-9a), 132.7 (C-7), 132.2 (C-8), 130.0 (C-2a), 123.1 (C-5a), 113.0 (C-9), 110.3 (C-6), 92.4 (C-10a), 25.1 (Me-3), 19.9 and 19.7 (Me-7 and Me-8), 15.0 ($COCH_3$); IR (KBr) 1700, 1660, 1650, 1590 cm^{-1}. Anal. Calcd for $C_{15}H_{16}N_4O_2$: C, 63.36; H, 5.67; N, 19.70. Found: C, 63.32; H, 5.46; N, 19.63.

(±)-3-Propyl-10-acetyl-4*H*,10*H*-azeto[3′,2′:4,5]pyrazolo[1,5-*a*]benzimidazol-2-one (2c): pink crystals, mp 197–198 °C dec (methanol); ^1H NMR (200 MHz, DMSO-d_6) δ 10.11 (s, 1 H,

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H-1), 7.77 (dd, J = 7.0, 1.3 Hz, 1 H, H-9), 7.53 (dd, J = 7.0, 1.33 Hz, 1 H, H-6), 7.40–7.25 (m, 2 H, H-7, H-8), 2.88 (t, J = 7.1 Hz, 2 H, CH_2), 2.27 (s, 3 H, $COCH_3$), 1.65 (m, 2 H, CH_2), 0.93 (t, J = 7.34 Hz, 3 H, CH_3); ^{13}C NMR (50 MHz, DMSO-d_6) δ 171.7 ($COCH_3$), 161.6 (C-2), 159.4 (C-3), 143.7 (C-9a), 131.2 (C-2a), 123.8 (C-7), 122.1 (C-8), 112.9 (C-9), 110.1 (C-6), 91.7 (C-10a), 30.7, 25.2 and 21.8 ($CH_2CH_2CH_3$), 14.1 ($COCH_3$); IR (KBr) 1680, 1660, 1590 cm^{-1}. Anal. Calcd for $C_{15}H_{16}N_4O_2O_2$: C, 63.36; H, 5.67; N, 19.70. Found: C, 63.58; H, 5.90; N, 19.69.

(±)-3-Propyl-7,8-dimethyl-10-acetyl-4*H*,10*H*-azeto-[3′,2′:4,5]pyrazolo[1,5-*a*]benzimidazol-2-one (2d): white crystals, mp 221–222 °C (methanol); ^1H NMR (300 MHz, DMSO-d_6) δ 12.08 (s, 1 H, H-4), 10.01 (s, 1 H, H-1), 7.58 (s, 1 H, H-9), 7.31 (s, 1 H, H-6), 2.85 (t, J = 7.1 Hz, 2 H, CH_2), 2.50 (s, 3 H, $COCH_3$), 2.34 (s, 3 H, Ar-Me), 2.29 (s, 3 H, Ar-Me), 1.70 (m, 2 H, CH_2), 0.95 (t, J = 7.34 Hz, 3 H, CH_3); ^{13}C NMR (50 MHz, DMSO-d_6) δ 171.4 ($COCH_3$), 161.3 (C-2), 158.5 (C-3), 143.0 (C-9a), 132.6 (C-7), 132.0 (C-8), 129.7 (C-2a), 123.0 (C-5a), 112.8 (C-6), 110.2 (C-9), 91.4 (C-10a), 36.5, 24.9, 21.5 ($CH_2CH_2CH_3$), 19.7 and 19.5 (Me-7 and Me-8), 13.89 ($COCH_3$); IR (KBr) 1685, 1655, 1585 cm^{-1}. Anal. Calcd for $C_{17}H_{20}N_4O_2$: C, 65.36; H, 6.45; N, 17.93. Found: C, 65.04; H, 6.74; N, 17.84.

2-Methyl-4-acetyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (3a): pink crystals, mp 161–162 °C (ethanol) (lit.[8] mp 160 °C).

2,6,7-Trimethyl-4-acetyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (3b): pink crystals, mp 186–187 °C (ethanol); ^1H NMR (60 MHz, $CDCl_3$) δ 7.9 (s, 1 H, H-5), 7.25 (s, 1 H, H-8), 5.65 (s, 1 H, H-3), 2.50 (s, 3 H, $COCH_3$), 2.35 (s, 3 H, Me-2), 2.25 (s, 6 H, Ar-Me); IR (KBr) 1705 cm^{-1}. Anal. Calcd for $C_{14}H_{15}N_3O$: C, 69.68; H, 6.26; N, 17.41. Found: C, 69.41; H, 6.34; N, 17.76.

2-Propyl-6,7-dimethyl-4-acetyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (3d): white crystals, mp 124–125 °C (ethanol); ^1H NMR (60 MHz, DMSO-d_6) δ 8.20 (s, 1 H, H-5), 8.00 (s, 1 H, H-8), 6.15 (s, 1 H, H-3), 2.85 (s, 3 H, $COCH_3$), 2.50 (t, J = 7.1 Hz, 2 H, CH_2), 1.75 (m, 2 H, CH_2), 0.98 (t, J = 7.34 Hz, 3 H, CH_3); IR (KBr) 1700 cm^{-1}. Anal. Calcd for $C_{16}H_{19}N_3O$: C, 71.34; H, 7.11; N, 15.60. Found: C, 71.02; H, 6.84; N, 15.36.

2-(Trifluoromethyl)-4-acetyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (3e): pink crystals, mp 175–176 °C (ethanol); ^1H NMR (300 MHz, DMSO-d_6) δ 8.36 (m, 1 H, H-5), 7.97 (m, 1 H, H-8), 7.52 (m, 2 H, H-6, H-7), 6.96 (s, 1 H, H-3), 2.72 (s, 3 H, $COCH_3$); IR (KBr) 1715 cm^{-1}. Anal. Calcd for $C_{12}H_8F_3N_3O$: C, 53.99; H, 3.02; N, 15.74. Found: C, 53.84; H, 3.14; N, 15.57.

2-(Trifluoromethyl)-6,7-dimethyl-4-acetyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (3f): white crystals, mp 205–206 °C (ethanol); ^1H NMR (60 MHz, DMSO-d_6) δ 8.05 (s, 1 H, H-5), 7.18 (s, 1 H, H-8), 6.85 (s, 1 H, H-3), 2.70 (s, 3 H, $COCH_3$), 2.40 (overlapped s, Ar-Me); IR (KBr) 1705 cm^{-1}. Anal. Calcd for $C_{14}H_{12}F_3N_3O$: C, 56.95; H, 4.09; N, 14.23. Found: C, 57.02; H, 4.17; N, 14.41.

2-Phenyl-4-acetyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (3g): brown crystals, mp 139–140 °C (ethanol); ^1H NMR (300 MHz, DMSO-d_6) δ 8.36 (m, 1 H, H-5), 8.00 (dd, 2 H, H-2′, H-6′), 7.83 (dd, 1 H, H-8), 7.52–7.36 (m, 5 H, Ar-H) 6.94 (s, 1 H, H-3), 2.74 (s, 3 H, $COCH_3$); IR (KBr) 1720 cm^{-1}. Anal. Calcd for $C_{17}H_{13}N_3O$: C, 74.16; H, 4.76; N, 15.26. Found: C, 74.23; H, 4.84; N, 15.54.

2,3-Tetramethylene-4-acetyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (3h): brown crystals, mp 135–136 °C dec (ethanol-water); ^1H NMR (300 MHz, DMSO-d_6) δ 8.03 (dd, J = 7.1 Hz, 1 H, H-5), 7.64 (dd, J = 7.85 Hz, 1 H, H-8), 7.34 (m, 2 H, H-6, H-7), 2.86 (m, 2 H, CH_2), 2.70 (s, 3 H, $COCH_3$), 2.51 (m, 2 H, CH_2), 1.74 (m, 4 H, CH_2CH_2); IR (KBr) 1700 cm^{-1}. Anal. Calcd for $C_{15}H_{15}N_3O$: C, 71.12; H, 5.96; N, 16.59. Found: C, 70.85; H, 6.25; N, 16.58.

2,3-Tetramethylene-6,7-dimethyl-4-acetyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (3i): white crystals, mp 169–170 °C (dimethylformamide); ^1H NMR (300 MHz, DMSO-d_6) δ 8.28 (s, 1 H, H-5), 8.12 (s, 1 H, H-8), 2.97 (s, 3 H, $COCH_3$), 2.85 (m, 2 H, CH_2), 2.49 (overlapped signal, CH_2), 2.35 (s, 6 H, Ar-Me), 1.78 (m, 4 H, CH_2CH_2); IR (KBr) 1710 cm^{-1}. Anal. Calcd for $C_{17}H_{19}N_3O$: C, 72.56; H, 6.80; N, 14.93. Found: C, 72.20; H, 6.55; N, 15.10.

2,3-Dimethyl-1-acetyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (4j): brown crystals, mp 138–139 °C (methanol-water); ^1H NMR (60 MHz, $CDCl_3$) δ 7.7 (m, 2 H, H-5, H-8), 7.25 (m, 2 H, H-6, H-7), 2.65 (s, 3 H, $COCH_3$), 2.35 (s, 3 H, Me), 2.25 (s, 3 H, Me); IR (KBr) 1695 cm^{-1}. Anal. Calcd for $C_{13}H_{13}N_3O$: C, 68.70; H, 5.76; N, 18.49. Found: C, 68.61; H, 5.90; N, 18.64.

2,3,6,7-Tetramethyl-1-acetyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (4k): white crystals, mp 262–263 °C dec (methanol); ^1H NMR (300 MHz, DMSO-d_6) δ 8.15 (s, 1 H, H-5), 7.24 (s, 1 H, H-8), 2.88 (s, 3 H, $COCH_3$), 2.35 (s, 6 H, Ar-Me), 2.30 (s, 3 H, Me), 2.05 (s, 3 H, Me); IR (KBr) 1710 cm^{-1}. Anal. Calcd for $C_{15}H_{17}N_3O$: C, 70.56; H, 6.71; N, 16.45. Found: C, 70.38; H, 6.40; N, 16.55.

Alkaline Hydrolysis of β-Lactams. β-Lactams **2** (1 mmol) were treated with 1 mequiv of 1 N sodium hydroxide solution in 95% ethanol at reflux temperature until complete disappearance of the starting materials. The solutions were evaporated, and the residues were dissolved in hot water and neutralized after cooling. The precipitated solids were recrystallized.

2-Methyl-4*H*-pyrazolo[1,5-*a*]benzimidazole-3-carboxamide (5a): white crystals, 58% yield, mp 273–274 °C dec (acetone); ^1H NMR (200 MHz, DMSO-d_6) δ 12.02 (s, 1 H, H-4), 7.71 (dd, J = 7.53, 1.0 Hz, 1 H, H-5), 7.48 (dd, J = 7.38, 1.0 Hz, 1 H, H-8), 7.27 (m, 2 H, H-6, H-7), 6.87 (ws, 2 H, NH_2), 2.50 (overlapped singlet, Me-2); IR (KBr) 3485, 3110, 1650, 1600 cm^{-1}. Anal. Calcd for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.70; N, 26.15. Found: C, 61.39; H, 4.90; N, 25.99.

2,6,7-Trimethyl-4*H*-pyrazolo[1,5-*a*]benzimidazole-3-carboxamide (5b): pink crystals, 70% yield, mp 284–285 °C dec (ethanol-water); ^1H NMR (300 MHz, DMSO-d_6) δ 7.51 (s, 1 H, Ar-H), 7.26 (s, 1 H, Ar-H), 6.79 (ws, 2 H, NH_2), 2.50 (overlapped singlet, Me-2), 2.33 (s, 3 H, Ar-Me), 2.32 (s, 3 H, Ar-Me); IR (KBr) 3700–2500, 1630, 1545 cm^{-1}. Anal. Calcd for $C_{13}H_{14}N_4O$: C, 64.44; H, 5.82; N, 23.12. Found: C, 64.11; H, 5.73; N, 22.29.

2-Propyl-4*H*-pyrazolo[1,5-*a*]benzimidazole-3-carboxamide (5c): white crystals, 65% yield, mp 211–212 °C (methanol); ^1H NMR (300 MHz), DMSO-d_6) δ 11.96 (s, 1 H, H-4), 7.72 (d, J = 7.5 Hz, 1 H, H-5), 7.47 (d, J = 7.5 Hz, 1 H, H-8), 7.23 (m, 2 H, H-6, H-7), 6.82 (ws, 2 H, NH_2), 2.89 (t, J = 7.8 Hz, 2 H, CH_2), 1.68 (m, 2 H, CH_2), 0.98 (t, J = 7.8 Hz, 3 H, CH_3); IR (KBr) 3375, 3320, 3150, 1650, 1590 cm^{-1}. Anal. Calcd for $C_{13}H_{14}N_4O$: C, 64.44; H, 5.82; N, 23.20. Found: C, 64.51; H, 5.93; N, 23.21.

2-Propyl-6,7-dimethyl-4*H*-pyrazolo[1,5-*a*]benzimidazole-3-carboxamide (5d): pink crystals, 60% yield, mp 225–226 °C dec (ethanol-water); ^1H NMR (300 MHz, DMSO-d_6) δ 11.73 (ws, 1 H, NH), 7.53 (s, 1 H, Ar-H), 7.27 (s, 1 H, Ar-H), 6.78 (ws, 2 H, NH_2), 2.90 (t, J = 7.34 Hz, 2 H, CH_2), 2.33 (s, 3 H, Ar-Me), 2.32 (s, 3 H, Ar-Me), 1.71 (m, 2 H, CH_2), 0.94 (t, J = 7.34 Hz, 3 H, CH_3); IR (KBr) 3335, 3300–2300, 1640, 1585 cm^{-1}. Anal. Calcd for $C_{15}H_{18}N_4O$: C, 66.64; H, 6.71; N, 20.72. Found: C, 66.45; H, 6.57; N, 20.92.

Acid Hydrolysis of Acetylpyrazolo[1,5-*a*]benzimidazoles. 4-Acetyl- and 1-acetylpyrazolo[1,5-*a*]benzimidazoles **3** and **4** (0.65 mmol) were dissolved in ethanol, and the solutions were refluxed in the presence of concentrated HCl (10 mL) for 30 min. The cooled reaction mixtures were neutralized with NaOH in ethanol. After filtration of any precipitated solids, the filtrates were evaporated and the solid residues recrystallized.

2-Methyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (6a): pink crystals, 96% yield, mp 246–247 °C (ethanol-water) (lit.[8] mp 247 °C).

2,6,7-Trimethyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (6b): white crystals, 98% yield, mp 246–247 °C (ethanol); ^1H NMR (60 MHz, DMSO-d_6) δ 11.0 (ws, 1 H, H-4), 7.30 (s, 1 H, Ar-H), 7.12 (s, 1 H, Ar-H), 5.52 (s, 1 H, H-3), 2.30 (overlapped s, 9 H, Me-2 and Ar-Me); IR (KBr) 1580 cm^{-1}. Anal. Calcd for $C_{12}H_{13}N_3$: C, 72.33; H, 6.57; N, 21.09. Found: C, 72.51; H, 6.65; N, 21.01.

2-Propyl-6,7-dimethyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (6d): white crystals, 60% yield, mp 251–252 °C (methanol); ^1H NMR (300 MHz, DMSO-d_6) δ 8.17 (s, 1 H, H-5), 7.27 (s, 1 H, H-8), 5.81 (s, 1 H, H-3), 2.50 (overlapped t, 2 H, CH_2), 2.34 (s, 6 H, Ar-Me), 1.70 (m, 2 H, CH_2), 0.94 (t, J = 7.34 Hz, 3 H, CH_3); IR (KBr) 1630, 1570 cm^{-1}. Anal. Calcd for $C_{14}H_{17}N_3$: C, 73.97; H, 7.53; N, 18.48. Found: C, 74.04; H, 7.38; N, 18.63.

2-(Trifluoromethyl)-4*H*-pyrazolo[1,5-*a*]benzimidazole (6e): white crystals, 85% yield, mp 244–246 °C (ethanol-water); ^1H NMR (300 MHz, DMSO-d_6) δ 11.90 (ws, 1 H, NH), 7.71 (dd, J = 8.0 Hz, 1 H, H-5), 7.56 (dd, J = 8.0 Hz, 1 H, H-8), 7.35 (m, 2 H, H-6, H-7), 6.37 (s, 1 H, H-3); IR (KBr) 1620, 1575 cm^{-1}. Anal. Calcd for $C_{10}H_6F_3N_3$: C, 53.33; H, 2.68; N, 18.66. Found: C, 53.19; H, 2.82; N, 18.61.

6,7-Dimethyl-2-(trifluoromethyl)-4*H*-pyrazolo[1,5-*a*]benzimidazole (6f): white crystals, 98% yield, mp 212–213 °C (methanol–water); ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.65 (ws, 1 H, NH), 7.69 (s, 1 H, H-5), 7.31 (s, 1 H, H-8), 6.29 (s, 1 H, H-3), 2.35 (s, 6 H, Ar-Me); IR (KBr) 1570 cm^{-1}. Anal. Calcd for $C_{12}H_{10}F_3N_3$: C, 56.98; H, 3.98; N, 16.16. Found: C, 57.00; H, 3.74; N, 16.55.

2,3-Tetramethylene-4*H*-pyrazolo[1,5-*a*]benzimidazole (6g): brown crystals, 80% yield, mp 287–288 °C dec (methanol–water); ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.20 (s, 1 H, NH), 7.60 (dd, J = 7.54 Hz, 1 H, H-5), 7.35 (dd, J = 7.54 Hz, 1 H, H-8), 7.15 (m, 2 H, H-6, H-7), 2.70 (m, 2 H, CH_2), 2.58 (m, 2 H, CH_2), 1.79 (m, 4 H, CH_2CH_2); IR (KBr) 1620 cm^{-1}. Anal. Calcd for $C_{13}H_{13}N_3$: C, 73.90; H, 6.20; N, 19.89. Found: C, 73.78; H, 6.18; N, 20.03.

2,3-Tetramethylene-6,7-dimethyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (6h): brown crystals, 92% yield, mp > 300 °C (methanol); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.16 (s, 1 H, H-5), 7.25 (s, 1 H, H-8), 2.61 (m, 2 H, CH_2), 2.50 (overlapped m, 2 H, CH_2), 2.33 (s, 6 H, Ar-Me), 1.74 (m, 4 H, CH_2CH_2); IR (KBr) 1650, 1570 cm^{-1}. Anal. Calcd for $C_{15}H_{17}N_3$: C, 75.27; H, 7.16; N, 17.56. Found: C, 75.48; H, 6.96; N, 17.38.

2,3-Dimethyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (6i): brown crystals, 85% yield, mp 299–300 °C dec (methanol); ^{1}H NMR (60 MHz, DMSO-d_6) δ 11.2 (ws, 1 H, H-4), 7.7 (m, 1 H, H-5), 7.3 (m, 3 H, H-6, H-7, H-8), 2.3 (s, 3 H, Me), 2.1 (s, 3 H, Me); IR (KBr) 1620 cm^{-1}. Anal. Calcd for $C_{11}H_{11}N_3$: C, 71.32; H, 5.98; N, 22.68. Found: C, 71.08; H, 6.09; N, 22.30.

2,3,6,7-Tetramethyl-4*H*-pyrazolo[1,5-*a*]benzimidazole (6j): brown crystals, 88% yield, mp > 300 °C (ethanol); ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.24 (s, 1 H, H-5), 6.88 (s, 1 H, H-8), 2.32 (s, 6 H, Ar-Me), 2.29 (s, 3 H, Me), 2.00 (s, 3 H, Me); IR (KBr) 1630 cm^{-1}. Anal. Calcd for $C_{13}H_{15}N_3$: C, 73.20; H, 7.08; N, 19.70. Found: C, 73.45; H, 6.96; N, 19.60.

Acknowledgment. This work was supported by the Spanish CICYT (PA86-0317). C. R. also is indebted to CONACYT and SEP (México) for a grant.

Registry No. **1a**, 91323-05-6; **1b**, 121361-06-6; **1c**, 130436-32-7; **1d**, 130436-33-8; **1e**, 130436-34-9; **1f**, 130436-35-0; **1g**, 130436-36-1; **1h**, 130436-37-2; **1i**, 130436-38-3; **1j**, 130436-39-4; **1k**, 130436-40-7; **1l**, 130436-41-8; **2a**, 130436-42-9; **2b**, 130436-43-0; **2c**, 130436-44-1; **2d**, 130436-45-2; **3a**, 53745-42-9; **3b**, 130436-46-3; **3d**, 130436-47-4; **3e**, 130436-48-5; **3f**, 130436-49-6; **3g**, 130436-50-9; **3h**, 130436-51-0; **3i**, 130436-52-1; **4j**, 130436-53-2; **4k**, 130436-54-3; **5a**, 130436-55-4; **5b**, 130436-56-5; **5c**, 130436-57-6; **5d**, 130436-58-7; **6a**, 22501-82-2; **6b**, 130436-59-8; **6d**, 130436-60-1; **6e**, 130436-61-2; **6f**, 130436-62-3; **6g**, 130436-63-4; **6h**, 130436-64-5; **6i**, 130436-65-6; **6j**, 130436-66-7; 1,2-diaminobenzimidazole, 29540-87-2; 5,6-dimethyl-1,2-diaminobenzimidazole, 60882-73-7; 1-amino-2-(methylamino)-benzimidazole, 107879-46-9.

Synthesis and Reactions of 1,3,4,6-Tetra-2-thienylthieno[3,4-*c*]thiophene

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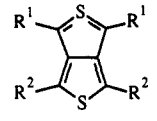
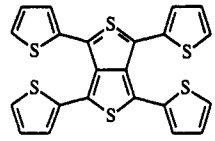
Received March 14, 1990

1,3,4,6-Tetra-2-thienylthieno[3,4-*c*]thiophene (**1f**) was synthesized from di-2-thenoylmethane after five steps. The cycloaddition reaction of **1f** with *N*-phenylmaleimide yielded a pair of exo (major) and endo (minor) adducts **7** and **8**, whose structures were assigned on the basis of the difference in the reactivity toward *m*-chloroperbenzoic acid. The reaction of **1f** with phenyl vinyl sulfoxide, dimethyl acetylenedicarboxylate, and di-2-thenoylacetylene gave benzo[*c*]thiophene derivatives **13**, **15**, and **16**, respectively.

Introduction

Although thieno[3,4-*c*]thiophenes, so-called "nonclassical" thienothiophenes, have been attracting much attention,[1] only a few thieno[3,4-*c*]thiophenes are known. The pioneering work in this field was done by Cava and co-workers, who reported the generation of transient 2,6-dimethyl (**1b**) and 2,6-bis(methoxycarbonyl) (**1c**)[2] and the synthesis of the first isolable 1,3,4,6-tetraphenyl derivatives (**1d**).[3] Afterward the synthesis and some reactions of an alternative type of thieno[3,4-*c*]-thiophenes, 1,3,4,6-tetrakis(alkylthio)thieno[3,4-*c*]-thiophenes (**1e**) were reported by Yoneda and co-workers.[4]





1a: $R^1 = R^2 = H$
b: $R^1 = CH_3$, $R^2 = H$
c: $R^1 = CO_2Me$, $R^2 = H$
d: $R^1 = R^2 = Ph$
e: $R^1 = R^2 = SR$

1f

Only recently we also reported the generation and characterization of the parent thieno[3,4-*c*]thiophene (**1a**).[5]

The title compound **1f** is of interest from the viewpoints of not only expanding the knowledge of thieno[3,4-*c*]-thiophenes but its chemical and physical properties because **1f** is formally composed by fusion of two molecules of α-terthiophenes at their central thiophene rings. α-Terthiophene is a compound of current interest due to its biological activities and as a starting material of electroconductive thiophene polymer.[6] We report here the

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