precipitated during refluxing (0.140 g, 0.700 mmol, 96%): mp 239–240 °C; ^{1}H NMR (acetone-d_6) δ 8.30 (s, 1 H), 8.67 (s, 1 H); ^{1}H NMR (Me_2SO-d_6) δ 7.77 (s, 2 H), 8.50 (s, 1 H), 8.87 (s, 1 H); ^{13}C NMR (acetone-d_6) δ 157.6, 148.1, 147.2, 116.1, 115.3, 113.1, 109.0, 103.3, 69.7; ^{13}C NMR (Me_2SO-d_6) δ 157.7 (s), 148.9 (d), 147.8 (d), 116.0 (s), 115.1 (s) 112.8 (s), 107.2 (s), 101.6 (s), 65.4 (s); IR (KBr) 3400 (NH_2, m), 3360 (NH_2, m), 3250 (NH_2, m), 3120 (w), 2215 (CN, s), 1670 (s), 1630 (w), 1565 (s) cm^{-1}; UV (CH_3CN) 408 (ε 27 500), 330 (7700), 320 (7400), 228 (22 900) nm; MS, *m/e* (relative intensity) 200 (M, 100), 173 (M – HCN, 94), 146 (M – C_3H_4N, 12.4), 121 (M – $C_4H_3N_2$, 11), 94 (M – $C_5H_4N_3$, 24). A pure sample was obtained by recrystallization from acetonitrile. Anal. Calcd for $C_9H_4N_4S$: C, 53.99; H, 2.01; N, 27.98; S, 16.01. Found: C, 53.79; H, 2.10; N, 27.84; S, 16.26.

Single-Crystal X-ray Diffraction Analysis of 2. Crystals of **2** suitable for X-ray diffraction could be grown from acetonitrile or methanol solutions by slow evaporation of the solvent. The crystal used in the determination was grown from methanol. Preliminary X-ray photographs displayed only triclinic symmetry, and accurate lattice constants of a = 12.205 (6) Å, b = 14.018 (5) Å, c = 3.836 (2) Å, α = 94.61 (3)°, β = 81.76 (4)°, and γ = 118.12 (3)° were determined from a least-squares fit of 15 moderate 2θ values. Density considerations indicated two molecules of composition $C_9H_4N_4S$ in the unit cell. Space group $P\bar{1}$ was assumed, and this was verified by successful refinement. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a computer-controlled four-circle diffractometer using a variable speed 1° ω scan and graphite-monochromated Cu K$\bar{\alpha}$ radiation (1.54178 Å). Of the 1575 reflections surveyed in this manner, 1050 (67%) were judged observed after correction for Lorentz, polarization, and background effects ($|F_o| \geq 3\sigma(F_o)$).[18] A phasing model was found by standard heavy atom techniques after the sulfur position was deduced from the Patterson synthesis. Hydrogen atoms and a methanol of crystallization were found in a difference electron density synthesis after partial refinement of the heavy atom positions. The current model has anisotropic heavy atoms and isotropic hydrogens and has been refined to a standard crystallographic residual of 0.070 for the observed reflections. Additional crystallographic parameters are available. Please consult the paragraph headed Supplementary Material Available for details.

Treatment of 5,5,6,6-Tetracyano-2-thiabicyclo[2.2.0]hexane with Anthracene in Refluxing Acetonitrile. 5,5,6,6-Tetracyano-2-thiabicyclo[2.2.0] hexane (1) (0.137 g, 0.685 mmol) and anthracene (0.178 g, 1.00 mmol) in acetonitrile (10 mL) were refluxed for 12 h. The color of the solution changed from pale yellow to violet after refluxing. When the solution was cooled, anthracene (0.030 g, 0.168 mmol) precipitated. The solvent was removed and methylene chloride (50 mL) was added to give a yellow precipitate (0.012 g, 0.060 mmol, 9%) that was identified as **2** from its mp, IR spectrum, and TLC behavior in comparison with authentic material. Removal of the solvent gave a brown solid (0.225 g) which was a mixture of at least three substances as indicated by thin-layer chromatography (methylene chloride/hexane, 1:1, silica gel): anthracene; 9,10-dihydro-9,10-ethanoanthracene-11,11,12,12-tetracarbonitrile, and a polar material at the origin. Column chromatography (methylene chloride/hexane, 1:1, silica gel, 100 g) was used to partially separate a mixture of anthracene and anthracene–TCNE adduct from the polar material. Anthracene and its TCNE adduct were then further separated by preparative TLC (methylene chloride/hexane, 1:1, silica gel): anthracene (0.10 g, 0.56 mmol); 9,10-dihydro-9,10-ethanoanthracene-11,11,12,12-tetracarbonitrile (0.072 g, 0.23 mmol, 34%). The spectroscopic properties and the melting point behavior [mp 264–268 °C dec; lit.[20] mp 268–270 °C dec] of the anthracene–TCNE adduct were identical with those of the authentic compound (mp 264–268 °C) that was synthesized independently from anthracene and tetracyanoethylene.[20] The polar material was removed from the column by elution with acetonitrile. Removal of the solvent gave a red, sticky solid (0.053 g).

Treatment of 5,5,6,6-Tetracyano-2-thiabicyclo[2.2.0]hexane with Anthracene in Refluxing Benzene. A mixture of 5,5,6,6-tetracyano-2-thiabicyclo[2.2.0]hexane (0.096 g, 0.480 mmol), anthracene (0.089 g, 0.500 mmol), and benzene (10 mL) was refluxed for 12 h. 3-Amino-4-cyano-2-(2,2-dicyanovinyl)thiophene (0.093 g, 0.465 mmol, 97%) precipitated during refluxing and was isolated by filtration and identified by its spectroscopic properties in comparison with those of the authentic compound. The anthracene was quantitatively recovered from the benzene filtrate.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research (S.A.M.-B. and D.C.D.). The X-ray crystallographic work (M.H.M.C. and J.C.) was supported by NIH Grant CA24487 and Bristol Laboratories. D.C.D. thanks Professor Larry Martin, Professor John Baldwin, and Professor Thomas J. Barton for helpful discussions.

Registry No. 1, 94732-90-8; **2**, 94732-91-9; 2*H*-thiete, 503-31-1; tetracyanoethylene, 670-54-2; 3-chlorothietane, 6013-95-2; anthracene, 120-12-7; 9,10-dihydro-9,10-ethanoanthracene-11,11,12,12-tetracarbonitrile, 1625-84-9.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances, and bond angles for compound **2** (4 pages). Ordering information is given on any current masthead page.

(20) Middleton, W. J.; Heckert, R. E.; Little, E. L.; Krespan, C. G. *J. Am. Chem. Soc.* **1968**, *80*, 2783.

C-Alkylation and N-Acylation of 4-Amino-1-azabutadiene Derivatives. A Convenient Route to Monoalkylated 1,3-Diketones

José Barluenga,* Jesús Jardón, and Vicente Gotor

Departamento de Química Orgánica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain

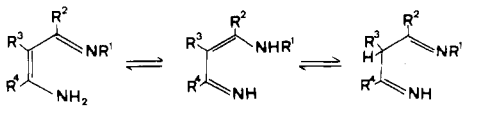
Received May 22, 1984

Alkylation of 4-amino-1-azabutadiene derivatives **1** with different alkyl halides followed by acid hydrolysis gives mono-C-alkylated 1,3-diketones **3** in excellent yields. In contrast acylation of **1** occurs at the imine nitrogen.

4-Amino-1-azabutadiene derivatives, **1**, are suitable starting materials for the synthesis of five- and six-membered heterocycles.[1]

Compounds **1** are easily obtained by reaction of Schiff bases with saturated nitriles in the presence of $AlCl_3$.[2]

Scheme I



1

Thus, 4-amino-1-azabutadienes **1** are prepared under mild conditions and high yields when R^3 = H, CH_3. The system

(1) (a) Barluenga, J.; Jardón, J.; Rubio, V.; Gotor, V. *J. Org. Chem.* **1983**, *48*, 1379. (b) Barluenga, J.; Rubio, V.; Gotor, V. *J. Org. Chem.* **1980**, *45*, 2592.

0022-3263/85/1950-0802$01.50/0

Table I. Compounds 2 from 1-Azabutadienes 1 and Alkyl Halides

no.	R^1	R^2	R^4	R^5	mp, °C[a]	yield, %
2a	C_6H_5	C_6H_5	C_6H_5	CH_3	162–164[b]	93
2b	C_6H_5	C_6H_5	p-$(CH_3)C_6H_4$	CH_2CH_3	140–141	83
2c	p-$(CH_3)C_6H_4$	C_6H_5	p-$(CH_3)C_6H_4$	CH_2CH_3	143–145	86
2d	p-$(CH_3)C_6H_4$	C_6H_5	c-C_6H_{11}	CH_2CH_3	138–40	90
2e	C_6H_5	C_6H_5	C_6H_5	$CH_2CH{=}CH_2$	94–95	85
2f	C_6H_5	C_6H_5	p-$(CH_3)C_6H_4$	$CH_2CH{=}CH_2$	129–131	91
2g	p-$(CH_3)C_6H_4$	C_6H_5	p-$(CH_3)C_6H_4$	$CH_2CH{=}CH_2$	135–137	91
2h	p-$(CH_3)C_6H_4$	C_6H_5	c-C_6H_{11}	$CH_2CH{=}CH_2$	122–123	94
2i	C_6H_5	C_6H_5	C_6H_5	$CH_2C_6H_5$	148–149	77
2j	C_6H_5	C_6H_5	p-$(CH_3)C_6H_4$	$CH_2C_6H_5$	170–172	93
2k	p-$(CH_3)C_6H_4$	C_6H_5	c-C_6H_{11}	$CH_2C_6H_5$	130–131	88
2l	p-$(CH_3)C_6H_4$	C_6H_5	C_6H_5	$CH_2C_6H_5$	170–171	92
2m	c-C_6H_{11}	H	p-$(CH_3)C_6H_4$	$CH_2C_6H_5$	105–107	78
2n	C_6H_5	C_6H_5	p-$(CH_3)C_6H_4$	$CH_2C{\equiv}CH$	156–158	76
2o	C_6H_5	C_6H_5	C_6H_5	$CH_2C{\equiv}CH$	136–138	86

[a] Satisfactory analytical data (C, ±0.3; H, ±0.25; N, ±0.3) were reported for all new compounds in the table. [b] Lit. mp 161–163 °C (see ref 2).

Table II. 1,3-Diketones 3 from Hydrolysis of 1-Azadienes 2

no.	R^2	R^5	R^4	mp, °C[a]	yield, %	^{13}C NMR
3a	C_6H_5	CH_3	C_6H_5	81–82[b]	85	49.9 (d), 196.8 (s)
3b	C_6H_5	CH_2CH_3	p-$(CH_3)C_6H_4$	oil	90	57.9 (d), 195.5 (s), 195.9 (d)
3c	C_6H_5	CH_2CH_3	c-C_6H_{11}	oil	88	61.2 (d), 192.8 (s), 195.3 (s)
3d	C_6H_5	$CH_2CH{=}CH_2$	p-$(CH_3)C_6H_4$	66–68	97	56.5 (d), 195.0 (s), 195.4 (s)
3e	C_6H_5	$CH_2CH{=}CH_2$	c-C_6H_{11}	oil	88	59.1 (d), 193.9 (s), 195.2 (s)
3f	C_6H_5	$CH_2C_6H_5$	p-$(CH_3)C_6H_4$	93–95	90	58.7 (d), 194.8 (s), 195.3 (s)
3g	C_6H_5	$CH_2C_6H_5$	C_6H_5	105–107	89	58.4 (d), 195.2 (s)
3h	C_6H_5	$CH_2C_6H_5$	c-C_6H_{11}	68–70	87	61.1 (d), 193.7 (s), 195.1 (s)
3i	C_6H_5	$CH_2C{\equiv}CH$	p-$(CH_3)C_6H_4$	oil	77	54.5 (d), 193.6 (s), 194.1 (s)

[a] Satisfactory analystical data (C, ±0.35; H, ±0.25) were reported for all new compounds in the table. [b] Lit. mp 82–83 °C (Weygand, C.; Forkel, H.; Bischoff, C. *Chem. Ber.* **1928**, *61B*, 687.)

Table III. *N*-Acyl-1-azadienes 4 and 5 from 1-Azadienes and Acyl Chlorides

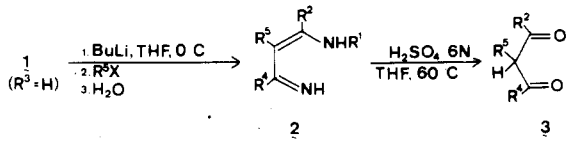
no.	R^1	R^2	R^4	R^6	mp, °C[a]	yield, %
4a	C_6H_5	C_6H_5	C_6H_5	C_6H_5	183–184	63
4b	C_6H_5	C_6H_5	p-$(CH_3)C_6H_4$	C_6H_5	170–172	61
4c	p-$(CH_3)C_6H_4$	C_6H_5	C_6H_5	C_6H_5	192–194	61
5a	C_6H_5	C_6H_5	C_6H_5	CH_3	161–162	70
5b	p-$(CH_3)C_6H_4$	C_6H_5	C_6H_5	CH_3	131–132	82
5c	C_6H_5	C_6H_5	p-$(CH_3)C_6H_4$	CH_3	129–131	75

[a] Satisfactory analytical data (C, ±0.3; H, ±0.15; N, ±0.2) were reported for all new compounds in the table.

1 may be seen as a masked 1,3-diketone since its hydrolysis yields 1,3-dicarbonyl compounds.[2] Having this in mind, we thought it worthwhile to study the behavior of 1 toward several alkylating and acylating agents in order to explore whether reaction would occur at the β-enamine carbon. If the reaction of 1 (R^3 = H) takes place in this way we would have a method for synthesizing 1-azabutadienes bearing an alkyl substituent at the 3-position. These intermediates should also be useful for preparing monoalkylated 1,3-diketones without undesirable side reactions, such as dialkylation, β-diketone cleavage,[3] or O-alkylation[4] which often occur by direct alkylation of 1,3-diketones.

It has been reported that imines derived from enolizable aldehydes and ketones react with alkyl halides, in the presence of organometallic compounds, giving rise to high yields of monoalkylated carbonyl compounds.[9] When 1 was allowed to react with an alkyllithium in THF at room temperature and then the corresponding alkyl halide was added, new azabutadiene derivatives 2 were isolated after hydrolysis (Scheme II, Table I). Alkylation at a position other than the β-enamine carbon or dialkylation products were not detected.[10]

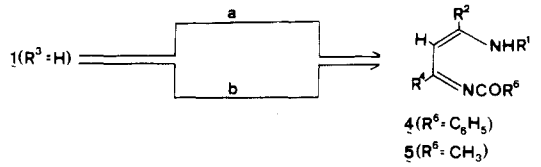
Scheme II



Compounds 2 were characterized by their elemental analyses and spectroscopic data. Of particular interest was the IR absorption at ca. 3350 cm^{-1} as well as the signal in ^{13}C NMR at δ 100 (singlet) which is assignable to the β-enamine carbon.[11]

(2) Hoberg, H.; Barluenga, J. *Synthesis* **1970**, 142.
(3) (a) House, H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: New York, 1972. (b) Carruthers, W. "Some Modern Methods of Organic Chemistry", 2nd ed.; Cambridge University Press: Cambridge, England, 1978.
(4) Among the methods reported to avoid the O-alkylation are those involving the presence of thallium(I) salts,[5,6] tetraalkylammonium fluorides,[7] and metal complexes.[8]
(5) Taylor, E. C.; Hawks, G. H., III; McKillop, A. *J. Am. Chem. Soc.* **1968**, *90*, 2421.
(6) Hooz, J.; Smith, J. *J. Org. Chem.* **1972**, *37*, 4200.
(7) (a) Clark, J. H.; Miller, J. M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1743. (b) Yamawaki, J.; Ando, T. *Chem. Lett.* **1979**, 755.
(8) Moreno-Mañas, M.; Trius, A. *Tetrahedron* **1981**, *37*, 3009.
(9) (a) Stork, G.; Dowd, S. R. *J. Am. Chem. Soc.*, **1963**, *85*, 2178. (b) Cuvigny, T.; Larchevêque, M.; Normant, H. *Liebigs Ann. Chem.* **1975**, 719.
(10) Only in a few cases mass spectra showed the crude reaction products to contain small amounts of the starting 1-azabutadiene.

Scheme III[a]



[a] (a) BuLi, THF, 0 °C; C_6H_5COCl; H_2O; (b) Py, THF, 0 °C; CH_3COCl; KOH 3 N.

Treatment of **2** with 6 N H_2SO_4 at 60 °C in THF resulted in the formation of the corresponding monoalkylated 1,3-diketones **3** in nearly quantitative yield (Table II). This sequence allows the C-alkylation of β-diketones in a selective manner suppressing the most usual competing reactions.

When **1** was treated with an alkyllithium and then benzoyl chloride the N-acylated products **4** were obtained. The ^{13}C NMR spectra of **4** display a signal at about 110 ppm (doublet) which can be assigned to the C_β-enamine carbon. Moreover, hydrolysis of **4c** with 6 N H_2SO_4 gave 1,3-diphenylpropane-1,3-dione, benzamide, and *p*-toluidine so one can state that the N-acylation takes place at the nonsubstituted nitrogen of the starting azadiene (Scheme III). Acylation of **1** with acetyl chloride to yield N-acetylated compounds **5** has been carried out with pyridine as base. *N*-acyl-1-azadienes are rarely found in the literature[12] and have been suggested as nonisolated intermediates in cycloaddition reactions.[13]

The fact that compounds **1** can be regioselectivity C-alkylated and N-acylated is in concordance with the HSAB principle[14] and is consistent with results in the literature concerning alkylation and acylation of 1,3-dicarbonyl compounds.[15]

Experimental Section

General Procedures. Melting points were taken on samples in open capillary tubes in a Büchi melting point apparatus and are uncorrected. The NMR spectra were obtained on a Varian FT-80 NMR spectrometer with deuterated chloroform as solvent, and shifts are reported in parts per million downfield (δ) from an internal tetramethylsilane (Me_4Si) standard. Infrared spectra were recorded in Nujol suspension on a Pye Unicam SP-1000 spectrophotometer. Mycroanalyses were performed on a Perkin-Elmer Model 240.

Compounds 2. General Procedure. 2-Allyl-3-imino-3-*p*-tolyl-1,*N*-diphenylprop-1-enamine (2f). An ethereal solution of butyllithium (6 mmol) was added under argon to a solution of 3-imino-3-*p*-tolyl-1,*N*-diphenylprop-1-enamine (1.56 g, 5 mmol) in 60 mL of dry THF at 0 °C. After stirring for 1 h, allyl bromide (0.51 mL, 6 mmol) was added dropwise. The solution was allowed to warm to room temperature and stirred for 14 h. The solution was slowly poured into ice-cooled water and extracted with three 50-mL portions of ether and the combined organic layers were dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by recrystallization from hot hexane to afford 1.60 g (91 %) of **2f**: mp 129–131 °C; IR (Nujol) ν_{max} 1610, 3410; ^1H NMR ($CDCl_3$, internal Me_4Si) δ 2.33 (s, CH_3), 2.64 (d, CH_2), 4.62 (m, $=CH_2$), 5.3 (m, =CH—), 6.50-7.43 (m, 14 H, arom); ^{13}C NMR ($CDCl_3$, internal Me_4Si) δ 21.1 (q), 34.4 (t), 101.2 (s), 114.0 (t), 121.6 (d), 121.9 (d), 127.3, 127.7, 127.9, 128.6, 128.8, 136.8 (s), 138.1 (s), 138.8 (d), 150.5 (s), 170.8 (s). Anal. Calcd for $C_{25}H_{24}N_2$: C, 85.19; H, 6.86; N, 7.95. Found: C, 85.03; H, 6.79; N, 7.90 (see paragraph at the end of paper about supplementary material).

1,3-Diketones 3. General Procedure. 2-Allyl-3-*p*-tolyl-1-phenyl-1,3-propanedione (3d). To a solution of **2f** (1g) in THF was added 30 mL of 6 N H_2SO_4 and the mixture was allowed to warm to 60 °C. After stirring for 5 h, the solution was slowly poured into ice-cooled water and extracted with ether. The dry organic layer was evaporated and the residue washed with hexane to afford 0.76 g (97 %) of **3d**: mp 66–68 °C; ^1H NMR ($CDCl_3$, internal Me_4Si) δ 2.37 (s, CH_3), 2.86 (t, CH_2), 4.85–5.40 (m, 3 H), 5.58–5.91 (m, =CH—), 7.10–8.08 (m, 9 H, arom); ^{13}C NMR ($CDCl_3$, internal Me_4Si) δ 21.4 (q), 33.4 (t), 56.5 (d), 116.9 (t), 128.4, 128.6, 129.4, 133.3 (d), 133.3 (s), 135.0 (s), 136.0 (s), 144.4 (s), 195.0 (s), 195.4 (s). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.36; H, 6.45 (see paragraph at the end of paper about supplementary material).

Products 4. General Procedure. *N*-(3-Anilino-3-phenyl-1-*p*-tolylprop-2-enylidene)benzamide (4b). **4b** was synthesized by the method described for **2f** and recrystallized from ethanol: mp 170–172 °C; IR (Nujol) ν_{max} 1630, 1705 cm^{-1}; ^1H NMR ($CDCl_3$, internal Me_4Si) δ 2.17 (s, CH_3), 5.7 (s, 1 H), 6.47–8.16 (m, 19 H, arom); ^{13}C NMR ($CDCl_3$, internal Me_4Si) δ 20.7 (q), 110.9 (d), 121.9 (d), 126.8, 127.1, 127.9, 128.1, 128.5, 128.9, 129.1, 132.0, 133.3, 134.0, 137.3 (s), 138.2 (s), 146.0 (s), 149.9 (s), 165.5 (s), 167.4 (s). Anal. Calcd for $C_{29}H_{24}N_2O$: C, 83.66; H, 5.82; N, 6.73. Found: C, 83.48; H, 5.80; N, 6.86.

Products 5. General Procedure. *N*-[3-(*p*-Methylanilino)-1,3-diphenylprop-2-enylidene]acetamide (5b). A solution of acetyl chloride (1.95 mL, 25 mmol) in 10 mL of THF was added dropwise to a stirred solution of 3-imino-1,3-diphenyl-*N*-*p*-tolylprop-1-enamine (1.56 g, 5 mmol) in 50 mL of THF and 10 mL of pyridine maintained below 5 °C by an ice bath. After stirring for 14 h, the reaction was slowly poured into ice cooled 3 N KOH and extracted with three 50-mL portions of ether. The dry organic layer was evaporated and the residue recrystallized from hexane/THF to afford 1.45 g (82%) of **5b**: mp 131–32 °C; IR (Nujol) ν_{max} 1640, 1720 cm^{-1}; ^1H NMR ($CDCl_3$, internal Me_4Si) δ 2.3 (s, CH_3), 2.6 (s, CH_3), 5.6 (s, 1 H), 6.6–8.0 (m, 14 H, arom), 13.2 (s, NH); ^{13}C NMR ($CDCl_3$, internal Me_4Si) δ 20.9 (q), 24.8 (q), 109.5 (d), 122.0 (d), 126.8, 127.4, 127.9, 128.1, 128.4, 128.8, 129.4, 133.4, 136.3 (s), 137.5 (s), 146.6 (s), 148.1 (s), 167.4 (s), 169.1 (s). Anal. Calcd for $C_{24}H_{22}N_2O$: C, 81.36; H, 6.26; N, 7.91. Found: C, 81.33; H, 6.22; N, 7.93.

Registry No. **1a**, 71115-31-6; **1b**, 78946-76-6; **1c**, 71443-43-1; **1d**, 73305-95-0; **1e**, 72923-08-1; **1m**, 94404-47-4; **2a**, 71115-28-1; **2b**, 94404-48-5; **2c**, 94404-49-6; **2d**, 94404-50-9; **2e**, 94404-51-0; **2f**, 94404-52-1; **2g**, 94404-53-2; **2h**, 94404-54-3; **2i**, 94404-55-4; **2j**, 94404-56-5; **2k**, 94404-57-6; **2l**, 94404-58-7; **2m**, 94404-59-8; **2n**, 94404-60-1; **2o**, 94404-61-2; **3a**, 1846-29-3; **3b**, 82145-68-4; **3c**, 94404-62-3; **3d**, 94404-63-4; **3e**, 94404-64-5; **3f**, 94404-65-6; **3g**, 28918-09-4; **3h**, 94404-66-7; **3i**, 94404-67-8; **4a**, 94404-68-9; **4b**, 94404-69-0; **4c**, 94404-70-3; **5a**, 94404-71-4; **5b**, 94404-72-5; **5c**, 94404-73-6; allyl bromide, 106-95-6; benzoyl chloride, 98-88-4; acetyl chloride, 75-36-5.

Supplementary Material Available: Complete IR, ^1H NMR, and ^{13}C NMR data for compounds **2**, **4**, and **5** and complete ^1H NMR and ^{13}C NMR data for compounds **3** (8 pages). Ordering information is given on any current masthead page.

(11) Stradi, R.; Trimarco, P.; Vivegani, A. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1.
(12) (a) Oppolzer, W.; Fröstl, W. *Helv. Chim. Acta* **1975**, *58*, 587. (b) Overman, L. E.; Clizbe, L. A.; Freerks, R. L.; Marlowe, C. K. *J. Am. Chem. Soc.* **1981**, *103*, 2807.
(13) Cheng, Y-S.; Lupo, A. T., Jr; Fowler, F. W. *J. Am. Chem. Soc.* **1983**, *105*, 7696.
(14) Pearson, J.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *89*, 1827.
(15) (a) Sarthou, P.; Guibé, F.; Bram, G. *J. Chem. Soc., Chem. Commun.* **1974**, 377. (b) Ono, N.; Yoshimura, T.; Saito, T.; Tamura, R.; Tanikaga, R.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1716.