# Synthesis of Pyrazole-Fused Heterocycles by Thermal Rearrangement of *N*-Aziridinylimino Ketenimines



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The reaction of *N*-aziridinylimino carboxamides **11** with a mixture of triphenylphosphine, carbon tetrachloride, and triethylamine in dichloromethane (Appel's condition) provides a new route to pyrazole-fused heterocycles such as 2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazoles **15** and 9,10-dihydro-4*H*-pyrazolo[5,1-*b*]-[1,3]benzodiazepines **17** *via* the thermal rearrangement of the expected *N*-aziridinylimino ketenimines **12**.

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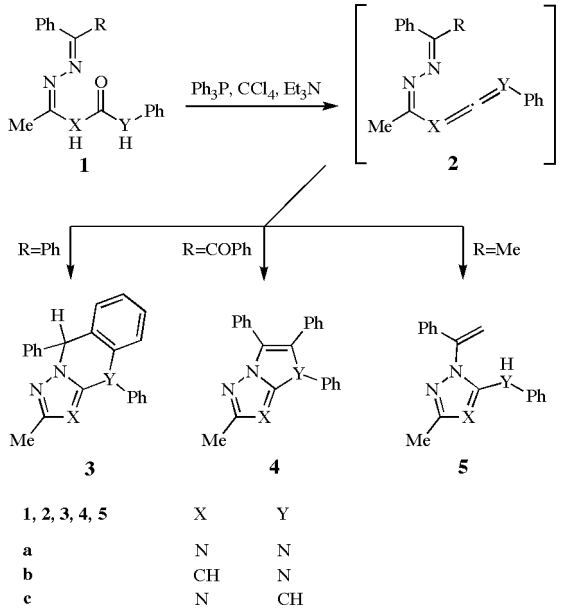
Recently, there has been a significant interest in the chemistry of *N*-aziridinylimines, which can be obtained by the reaction of 1-aminoaziridines with carbonyl compounds. $\beta$-Fragmentation of aziridine rings is a facile process due to the relief of ring strain originally explored by Eschenmoser [1]. This method has been studied for the preparations of acetylenic carbonyl compounds [1], Shapiro-like olefinations [2,3], carbonyl-to-methylene conversion [4], generation of carbenes [5], formation of allylic alcohols [6], and radical cyclizations [7].

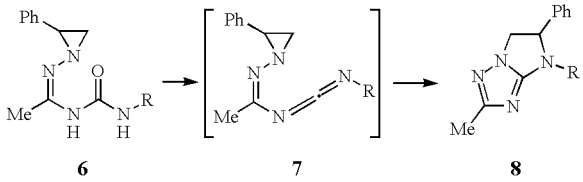
Also, the electrocyclic reaction of conjugated heterocumulenes as a synthetic route to heterocycles [8] prompts us to report on our studies. We recently described a new route to 1,2,4-triazole- or pyrazole-fused heterocycles such as 5,10-dihydro-1,2,4-triazolo[5,1-*b*]quinazolines **3a** [9], 7*H*-imidazo[1,2-*b*][1,2,4]triazoles **4a** [10], monocyclic *N*-$\alpha$-styryl-1,2,4-triazoles **5a** [11], 4,9-dihydropyrazolo-[5,1-*b*]quinazolines **3b** [12], 1*H*-imidazo[1,2-*b*]pyrazoles **4b** [12], monocyclic *N*-$\alpha$-styrylpyrazoles **5b** [12], and 5,10-dihydro-1,2,4-triazolo[1,5-*b*]isoquinolines **3c** [13], involving thermal rearrangement of azino carbodiimides **2a** or azino ketenimines **2b** or **2c** obtained from the corresponding azino ureas **1a** or the azino carboxamides **1b** or **1c** using Appel's dehydration method [14] (Scheme I). Similarly, thermal reaction of *N*-aziridinylimino carbodiimides **7** derived from dehydration of *N*-aziridinylimino ureas **6** lead to 5,6-dihydro-7*H*-imidazo[1,2-*b*][1,2,4]triazoles **8** [15] (Scheme II). We now wish to report that *N*-aziridinylimino ketenimines **12**, which are obtainable from the corresponding carboxamides **11** in the Appel's dehydration condition, give pyrazole-fused heterocycles **15** and **17** by thermal rearrangement (Scheme III).

Scheme I



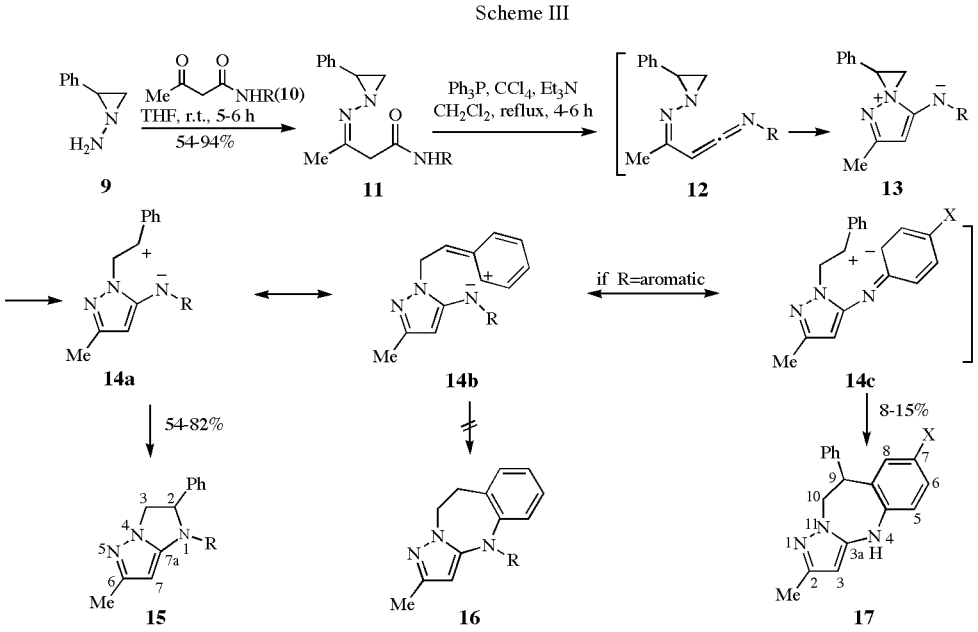

| 1, 2, 3, 4, 5 | X | Y |
|---|---|---|
| a | N | N |
| b | CH | N |
| c | N | CH |

Scheme II



The starting *N*-aziridinylimino carboxamides **11** were prepared by the reaction of 1-amino-2-phenylaziridine **9** [16] with acetoacetamide derivatives **10** in tetrahydrofuran at room temperature, respectively. Treatment of **11a-e** with triphenylphosphine, carbon tetrachloride, and triethylamine in dichloromethane at reflux temperature led to the formation of two products that were separated by column chromatography. The major product was isolated as a white solid and assigned as a 2,3-dihydro-1*H*-imidazo [1,2-*b*]-pyrazoles **15a-e** (54-82%) on the basis of the following spectral [17] and analytical data. A pyrazole ring was indicated by peaks at $\delta$ = 149.6-151.0 (C6), 84.8-86.2 (C7), and 154.1-154.8 (C7a) in the $^{13}$C NMR spectra of *N*-aryl compounds **15a-d**. There was also a C6-methyl absorption at $\delta$ = 14.8-15.4, as well as peaks at $\delta$ = 67.7-68.9 (C2) and 54.4-54.9 (C3) for the dihydroimidazole ring. In the $^{1}$H NMR spectra, the characteristic chemical shift of the methine protons of C2 and C7 were found at $\delta$ = 5.47-5.64 as a doublet and doublet and at $\delta$ = 5.56-5.68 as a singlet, and two methylene protons of C3 were observed at $\delta$ = 3.98-4.04 as a doublet and doublet and $\delta$ = 4.63-4.73 as a doublet and doublet, and proved to be correlated to the C3 carbon atom ($\delta$ = 54.4) by the two dimensional

Scheme III




| 10,11,15 | R | 17 | X |
|---|---|---|---|
| a | $C_6H_5$ | a | H |
| b | 4-$ClC_6H_4$ | b | Cl |
| c | 4-$MeC_6H_4$ | c | Me |
| d | 4-$MeOC_6H_4$ | d | MeO |
| e | $CH_3$ | | – |

carbon-proton heteronuclear correlation spectroscopy (HETCOR) of **15a**. On the other hand, the $^1$H NMR of *N*-methyl compound **15e** showed peaks at $\delta$ = 3.81, 4.42, and 4.61 as three triplets assignable to the dihydroimidazole ring, and the $^{13}$C NMR exhibited similar absorptions at $\delta$ = 153.7 (C6), 82.4 (C7), 156.3 (C7a), 72.9 (C2), 54.2 (C3), 14.6 ($C6CH_3$), and 35.7 ($NCH_3$).

The minor product was isolated as a white solid and was found to be the 9,10-dihydro-4*H*-pyrazolo[5,1-*b*][1,3]benzodiazepines **17** [18]. The $^{13}$C NMR showed peaks at $\delta$ = 148.8 (C3a), 142.7-144.2 (C2) and 97.8 (C3) assignable to the pyrazole ring and $\delta$ = 54.9-55.1 (C10) and 61.7-61.8 (C9) for the dihydrobenzodiazepine ring, in addition to the aromatic and methyl peaks. In the $^1$H NMR spectra, the chemical shift of the methine proton of C9 was found at $\delta$ = 5.35-5.38 as a triplet and two methylene protons of C10 were observed at $\delta$ = 4.34-4.36 and $\delta$ = 4.56-4.58 as doublet and doublet respectively, and NH protons were exhibited $\delta$ = 5.78-5.79 as a singlet and disappeared by deuterium exchange experiment. Also the infrared spectra of **17a** and **17b** showed absorptions at 3238 and 3226 cm$^{-1}$ due to the secondary amino group.

A reasonable mechanism for the transformation of **11** into **15** and **17** is shown in Scheme III. The presumed intermediate *N*-aziridinylimino ketenimines **12** were too unstable to isolate, so the thermal reactions of **12** would give the zwitterionic aziridinum ion **13** followed by aziridine ring opening to give the resonance-stabilized zwitterionic intermediates **14a-c** and subsequent ring closure and/or rearomatization would give the products **15** and **17**. No pyrazolobenzodiazepines **16** were produced in this reaction.

In conclusion, the facility of *N*-aziridinylimino carboxamides for the synthesis of pyrazole-fused heterocycles *via* the tandem Appel's dehydration/thermal rearrangement method was achieved under mild reaction conditions.

## EXPERIMENTAL

All reagents and solvents were reagent grade or were purified by standard methods before use and the reactions were routinely carried out under an inert atmosphere. Silica gel 60 (70-230 mesh ASTM) used for column chromatography was supplied by E. Merck. Analytical thin layer chromatography (tlc) was performed on silica gel with fluorescent indicator coated on aluminium sheets. Melting points were taken using an Electrothermal melting point apparatus and are uncorrected. Microanalyses were obtained using a Carlo Erba EA 1180 element analyzer. Mass spectra were obtained using a ThermoQuest Polaris Q mass spectrometer operating at 70 eV. Infrared spectra were recorded on a Nicolet Magna 550 FTIR spectrometer. The $^1$H and $^{13}$C nmr spectra were measured on a Gemini 300 spectrometer. All chemical shifts are reported in parts per million (δ) relative to tetramethylsilane.

Table 1

3-(2-Phenylaziridin-1-ylimino)butyramides **11a-e**

| | Reaction Time (h) | Yield (%) | MP (°) | Molecular Formula | Analysis (%) Calcd./Found C | H | N | $^1$H NMR δ (ppm), J (Hz) (Deuterochloroform) |
|---|---|---|---|---|---|---|---|---|
| **11a** | 5 | 90 | 59-61 | $C_{18}H_{19}N_3O$ | 73.70 | 6.53 | 14.32 | 2.13 (s, 3H, $CH_3$), 2.41 (d, 1H, J = 4.5, $CH_2$), 2.50 (d, 1H, J = 7.5, $CH_2$), 2.95 (dd, 1H, J = 7.5, J = 4.5, CH), 3.34 (s, 2H, $CH_2$), 6.98-7.35 (m, 10$H_{arom}$), 9.19 (s, 1H, NH) |
| | | | | (293.4) | 73.51 | 6.89 | 13.99 | |
| **11b** | 5 | 92 | 70-71 | $C_{18}H_{18}ClN_3O$ | 65.95 | 5.53 | 12.81 | 2.12 (s, 3H, $CH_3$), 2.42 (d, 1H, J = 4.8, $CH_2$), 2.49 (d, 1H, J = 7.5, $CH_2$), 2.95 (dd, 1H, J = 7.5, J = 4.8, CH), 3.34 (s, 2H, $CH_2$), 6.88 (d, J = 7.2, 2$H_{arom}$), 7.06-7.35 (m, 5$H_{arom}$), 7.48 (d, J = 7.2, 2$H_{arom}$), 9.26 (s, 1H, NH) |
| | | | | (327.8) | 66.21 | 5.61 | 12.61 | |
| **11c** | 6 | 90 | 96-97 | $C_{19}H_{21}N_3O$ | 74.24 | 6.89 | 13.67 | 2.13 (s, 3H, $CH_3$), 2.32 (s, 3H, $CH_3$), 2.41 (d, 1H, J = 4.5, $CH_2$), 2.49 (d, 1H, J = 7.5, $CH_2$), 2.94 (dd, 1H, J = 7.5, J = 4.5, CH), 3.32 (s, 2H, $CH_2$), 7.11-7.40 (m, 9$H_{arom}$), 9.09 (s, 1H, NH) |
| | | | | (307.4) | 73.88 | 7.09 | 13.34 | |
| **11d** | 5 | 94 | 81-82 | $C_{19}H_{21}N_3O_2$ | 70.57 | 6.55 | 12.99 | 2.13 (s, 3H, $CH_3$), 2.41 (d, 1H, J = 4.5, $CH_2$), 2.49 (d, 1H, J = 7.8, $CH_2$), 2.94 (dd, 1H, J = 7.8, J = 4.5, CH), 3.32 (s, 2H, $CH_2$), 3.79 (s, 3H, $OCH_3$), 6.85 (d, J = 8.7, 2$H_{arom}$),7.26-7.33 (m, 5$H_{arom}$),7.42 (d, J = 8.7, 2$H_{arom}$), 9.01 (s, 1H, NH) |
| | | | | (323.4) | 70.32 | 6.87 | 12.92 | |
| **11e** | 6 | 65 | oil | $C_{13}H_{17}N_3O$ | 67.51 | 7.41 | 18.17 | 2.07 (s, 3H, $CH_3$), 2.34 (d, 1H, J = 4.7, $CH_2$), 2.56 (d, 1H, J = 7.5, $CH_2$), 2.79 (d, 3H, J = 4.7, $NCH_3$), 2.90 (dd, 1H, J = 7.5, J = 4.7, CH), 3.15 (s, 2H, $CH_2$), 6.73 (br s, 1H, NH), 7.22-7.37 (m, 5$H_{arom}$) |
| | | | | (231.3) | 67.73 | 7.73 | 18.46 | |

Table 2

Pyrazole-Fused Heterocycles **15** and **17** Prepared under Appel's Conditions

| Reactant | Reaction Time (h) | Product | Yield (%) | MP (°) | Molecular Formula | Analysis (%) Calcd./Found C | H | N | IR(KBr) ν ($cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| **11a** | 4 | **15a** | 66 | 100-101 | $C_{18}H_{17}N_3$ | 78.52 | 6.22 | 15.26 | 1588, 1558, 1512, 1389 |
| | | | | | (275.3) | 78.70 | 6.40 | 15.40 | |
| | | **17a** | 8 | 96-98 | $C_{18}H_{17}N_3$ | 78.52 | 6.22 | 15.26 | 3238, 1606, 1559, 1499 |
| | | | | | (275.3) | 78.45 | 5.96 | 14.93 | |
| **11b** | 5 | **15b** | 54 | 102-103 | $C_{18}H_{16}ClN_3$ | 69.79 | 5.20 | 13.56 | 1600, 1554, 1516, 1393 |
| | | | | | (309.8) | 69.94 | 5.34 | 13.21 | |
| | | **17b** | 15 | 102-104 | $C_{18}H_{16}ClN_3$ | 69.79 | 5.20 | 13.56 | 3226, 1606, 1558, 1495 |
| | | | | | (309.8) | 69.48 | 5.07 | 13.28 | |
| **11c** | 6 | **15c** | 62 | 112-113 | $C_{19}H_{19}N_3$ | 78.86 | 6.62 | 14.52 | 1622, 1562, 1524, 1347 |
| | | | | | (289.4) | 79.11 | 6.82 | 14.84 | |
| **11d** | 6 | **15d** | 78 | 121-122 | $C_{19}H_{19}N_3O$ | 74.73 | 6.27 | 13.76 | 1588, 1561, 1518, 1390 |
| | | | | | (305.4) | 74.38 | 6.42 | 13.86 | |
| **11e** | 4 | **15e** | 82 | 82-83 | $C_{13}H_{15}N_3$ | 73.21 | 7.09 | 19.70 | 1571, 1457, 1389, 1296 |
| | | | | | (213.3) | 73.14 | 7.34 | 19.92 | |

Acetoacetanilides **10a**, **10b** and **10d** were purchased from Aldrich Chemical Co. 1-Amino-2-phenylaziridine [16], *p*-acetoacetotoluidide (**10c**) [19], and *N*-methyl acetoacetamide (**10e**) [20] were prepared following the literature procedures.

*N*-Aryl-3-(2-phenylaziridin-1-ylimino)butyramides (**11a-d**) and *N*-Methyl-3-(2-phenylaziridin-1-ylimino)butyramide (**11e**).

General Procedure.

To a stirred solution of acetoacetamide derivatives (**10**, 10 mmoles) in 20 ml of tetrahydrofuran was added 1-amino-2-phenylaziridine (**9**, 1.34 g, 10 mmoles) at room temperature. The mixture was stirred at room temperature for 5-6 hours, and the resulting solution was concentrated to dryness. The residue was crystallized from ether/hexane to give the products **11** as white solids.

The physical and spectral data of **11** prepared by this general method are listed in Table 1.

6-Methyl-2-phenyl-2,3-dihydro-1*H*-imidazo[1,2-*b*]pyrazoles **15a-e**, 2-Methyl-9-phenyl-9,10-dihydro-4*H*-pyrazolo[5,1-*b*]-[1,3]benzodiazepine (**17a**) and 7-Chloro-2-methyl-9-phenyl-9,10-dihydro-4*H*-pyrazolo[5,1-*b*][1,3]benzodiazepine (**17b**).

General procedure.

To a stirred solution of the appropriate carboxamide (**11**, 3 mmoles) in 20 ml of dichloromethane was added triphenyl-

Table 3

NMR and Mass Spectra Data of Compounds **15** and **17**

| | $^1$H NMR δ (ppm), J (Hz) (Deuterochloroform) | $^{13}$C NMR δ (ppm) (Deuterochloroform) | Mass Spectra m/z (%) |
|---|---|---|---|
| **15a** | 2.31 (s, 3H, $CH_3$), 4.04 (dd, 1H, J = 9.6, J = 5.6, C3H), 4.72 (dd, 1H, J = 9.6, J = 9.2, C3H), 5.64 (dd, 1H, J = 9.2, J = 5.6, C2H), 5.68 (s, 1H, C7H), 6.86-6.96 (m, 3$H_{arom}$), 7.19-7.34 (m, 7$H_{arom}$) | 14.9, 54.4, 67.7, 85.7, 115.0, 120.6, 126.0, 128.3, 129.2, 129.3, 140.3, 141.3, 149.6, 154.1 | 275 ($M^+$, 100), 274 (21), 184 (10), 173 (38) |
| **15b** | 2.32 (s, 3H, $CH_3$), 4.05 (dd, 1H, J = 9.3, J = 5.6, C3H), 4.73 (dd, 1H, J = 9.3, J = 9.3, C3H), 5.61 (dd, 1H, J = 9.3, J = 5.6, C2H), 5.65 (s, 1H, C7H), 6.87 (d, J = 8.2, 2$H_{arom}$), 7.17 (d, J = 8.2, 2$H_{arom}$), 7.28-7.33 (m, 5$H_{arom}$) | 15.4, 54.8, 68.4, 86.2, 116.8, 126.2, 126.5, 129.1, 129.7, 129.9, 140.2, 140.3, 149.7, 154.8 | 311 (35), 309 ($M^+$, 100), 294 (11), 209 (13), 207 (43) |
| **15c** | 2.25 (s, 3H, $CH_3$), 2.31 (s, 3H, $CH_3$), 4.03 (dd, 1H, J = 9.4, J = 5.9, C3H ), 4.71 (dd, 1H, J = 9.4, J = 9.0, C3H), 5.61 (dd, 1H, J = 9.0, J = 5.9, C2H ), 5.64 (s, 1H, C7H), 6.86 (d, J = 8.2, 2$H_{arom}$), 7.03 (d, J = 8.2, 2$H_{arom}$), 7.29–7.34 (m, 5$H_{arom}$) | 15.4, 21.1, 54.9, 68.5, 85.9, 115.9, 126.7, 128.8, 129.8, 130.3, 130.8, 139.6, 140.8, 150.7, 154.7 | 290 ($M^+$, 22), 289 (100), 288 (18), 198 (14), 187 (38) |
| **15d** | 2.30 (s, 3H, $CH_3$), 3.67 (s, 3H, $OCH_3$), 3.98 (dd, 1H, J = 9.6, J = 6.7, C3H), 4.63 (dd, 1H, J = 9.6, J = 9.3, C3H), 5.47 (dd, 1H, J = 9.3, J = 6.7, C2H), 5.56 (s, 1H, C7H), 6.75 (d, J = 8.7, 2$H_{arom}$), 6.90 (d, J = 8.7, 2$H_{arom}$), 7.24–7.32 (m, 5$H_{arom}$) | 14.8, 30.9, 54.5, 68.9, 84.8, 114.6, 117.5, 126.4, 128.4, 129.2, 135.4, 140.0, 151.0, 154.1, 154.4 | 305 ($M^+$, 100), 304 (8), 290 (32), 214 (11), 203 (15) |
| **15e** | 2.24 (s, 3H, $CH_3$), 2.63 (s, 3H, $CH_3$), 3.81 (t, 1H, J = 10.0, C3H), 4.42 (t, 1H, J = 9.0, C3H), 4.61 (t, 1H, J = 9.8, C2H), 5.19 (s, 1H, C7H), 7.35–7.42 (m, 5$H_{arom}$) | 14.6, 35.7, 54.2, 72.9, 82.4, 127.4, 128.4, 128.6, 137.5, 153.7, 156.3 | 213 ($M^+$, 100), 212 (30), 198 (8), 111 (20) |
| **17a** | 2.29 (s, 3H, $CH_3$), 4.34 (dd, 1H, J = 14.2, J = 6.6, C10H), 4.56 (dd, 1H, J = 14.2, J = 7.6, C10H), 4.81 (s, 1H, C3H), 5.35 (dd, 1H, J = 7.6, J = 6.6, C9H), 5.78 (s, 1H, NH), 6.65-7.23 (m, 4$H_{arom}$), 7.38 (br s, 5$H_{arom}$) | 14.2, 54.9, 61.7, 97.8, 115.1, 120.4, 127.4, 128.9, 129.1, 129.4, 138.6, 142.1, 144.2, 148.8 | 275 ($M^+$, 100), 274 (23), 173 (39), 143 (12), 117 (16), 103 (29), 77 (58) |
| **17b** | 2.32 (s, 3H, $CH_3$), 4.36 (dd, 1H, J = 14.2, J = 6.7, C10H), 4.58 (dd, 1H, J = 14.2, J = 7.8, C10H), 4.85 (s, 1H, C3H), 5.38 (dd, 1H, J = 7.8, J = 6.7, C9H), 5.79 (s, 1H, NH), 6.62 (d, J = 8.8, 2$H_{arom}$), 7.18 (d, J = 8.8, 2$H_{arom}$), 7.42 (s, 4$H_{arom}$) | 14.1, 55.1, 61.8, 97.8, 116.2, 124.9, 127.2, 127.5, 129.0, 129.3, 138.3, 141.7, 142.7, 148.8 | 311 (36), 309 ($M^+$, 100), 294 (9), 218 (10), 209 (20), 207 (60) |

phosphine (0.79 g, 3 mmoles), carbon tetrachloride (0.58 ml, 6 mmoles), and triethylamine (0.42 ml, 3 mmoles) at room temperature. The mixture was heated at reflux temperature for 3 hours, and the same amount of triphenylphosphine, carbon tetrachloride, and triethylamine was added again. The resulting solution was then stirred at reflux temperature for 1-3 hours more, and poured into water (30 ml) and extracted with dichloromethane (2 × 30 ml). The organic layer was separated, dried over magnesium sulfate, and concentrated to dryness *in vacuo*. The residue was chromatographed on a silica gel column eluting with hexane/ethyl acetate (5:1) to give the products **15** and **17** as white solids.

The physical and spectral data of **15** and **17** prepared by this general method are listed in Table 2 and Table 3.

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REFERENCES AND NOTES

[*] Author to whom correspondence should be addressed.

[1] D. Felix, R. K. Muller, U. Horn, R. Joos, J. Schreiber and A. Eschenmoser, *Helv. Chim. Acta*, **55**, 1276 (1972).

[2] D. A. Evans and J. V. Nelson, *J. Am. Chem. Soc*., **102**, 774 (1980).

[3] F. Mohamadi and D. B. Collum, *Tetrahedron Lett*., **25**, 271 (1984).

[4] C. L. Leone and A. R. Chamberin, *Tetrahedron Lett*., **32**, 1691 (1991).

[5] A. Padwa, Y. Gareau and S. L. Xu, *Tetrahedron Lett*., **32**, 983 (1991).

[6] H, -Y. Kang, W. S. Hong, S. H. Lee, K. I. Choi and H. Y. Koh, *Synlett*, 33 (1997).

[7a] S. Kim, I. S. Kee and S. Lee, *J. Am. Chem. Soc*., **113**, 9882 (1991); [b] S. Kim and I. S. Kee, *Tetrahedron Lett*., **34**, 4213 (1993); [c] H. -Y. Lee, D. -I. Kim and S. Kim, *J. Chem. Soc. Chem. Commun*., 1539 (1996); [d] S. Kim and J. H. Cheong, *Synlett*, 947 (1997).

[8a] J. Barluenga and F. Palacios, *Org. Prep. Proced. Int*., **23**, 1 (1991); [b] N. I. Gusar, *Russ. Chem. Rev*., **60**, 146 (1991); [c] Y. G. Gololobov and L. F. Kasukhin, *Tetrahedron*, **48**, 1353 (1992); [d] S. Eguchi, Y. Matsushita and K. Yamashita, *Org. Prep. Proced. Int*., **24**, 209 (1992); [e] P. Molina and M. J. Vilaplana, *Synthesis*, 1197 (1994); [f] H. Wamhoff, G. Richardt and S. Stölben, In Advances in Heterocyclic Chemistry, Vol. **64**, A. R. Katritzky, ed, Academic Press, Orlando (FL), 1995, pp 159.

[9] K. -J. Lee, S. H. Kim, S. Kim, H. Park, Y. R. Cho, B. Y. Chung and E. E. Schweizer, *Synthesis*, 1057 (1994).

[10] K. -J. Lee, D. -H. Song, D. -J. Kim and S. -W. Park, *J. Heterocyclic Chem*., **33**, 1877 (1996).

[11] K. -J. Lee, Y. -S. Lee and D. -H. Song, *Bull. Korean Chem. Soc*., **16**, 1037 (1995).

[12] K. -J. Lee, H. -T. Kwon and B. -G. Kim, *J. Heterocyclic Chem*., **34**, 1795 (1997).

[13] K. -J. Lee, S. H. Kim and J. H. Kwon, *Synthesis*, 1461 (1997).

[14] R. Appel, R. Kleinstück and K. -D. Ziehn, *Chem. Ber*., **104**, 1335 (1971).

[15] K. -J. Lee and S. -U. Kang, *Tetrahedron Lett*., **36**, 2815 (1995).

[16] R. K. Muller, R. Joos, D. Felix, J. Schreiber, C. Wintner and A. Eschenmoser, *Org. Synth*., **55**, 114 (1976).

[17] Numberings are shown in scheme III.

[18] A tiny amount of production of the minor product **17c** and **17d** was indicated by thin layer chromatography, however, isolation was unsuccessful.

[19] C. F. Kaslow and N. B. Sommer, *J. Am. Chem. Soc.*, **68**, 644 (1946).

[20] D. Bormann, In Methoden der Organsichen Chemie (Houben-Weyl-Müller), 4, Aufl., Bd. VII / 4, S. 233; Thieme: Stuttgart, 1968.

[21] Y. Yamamoto, S. Ohnishi and Y. Azuma, *Synthesis*, 122 (1981).