Application of the Intramolecular Aza-Wittig Reaction to the Synthesis of Vinylogous Urethanes and Amides

P. H. Lambert, M. Vaultier, and R. Carrié*

Groupe de Recherches de Physicochimie Structurale, U.A. CNRS No. 704, Université de Rennes I, 35042 Rennes Cedex, France

Received February 11, 1985

The treatment of ω-azido β-dicarbonyl derivatives with 1 equiv of triphenylphosphine leads to a transient phosphinimine (Staudinger reaction), which cyclizes into vinylogous urethanes and amides via an intramolecular aza-Wittig reaction in excellent yields. The starting azides were obtained by a nucleophilic substitution by NaN_3 in Me_2SO on the corresponding ω-halo β-dicarbonyl derivatives that were accessible by the γ-alkylation of β-dicarbonyl compounds with α,ω-dihaloalkanes.

Vinylogous urethanes **1** constitute a valuable class of intermediates used for the synthesis of alkaloids such as pyrrolizidines,[1] indolizidines,[2] and quinolizidines.[3] An established method for preparing these compounds is the elegant sulfide contraction procedure developed by the Eschenmoser group.[4] Other interesting syntheses of these molecules were recently developed via (methylthio)alkylideniminium salts **2**[5] or lactam derivatives **3–5**[6] (Chart I).

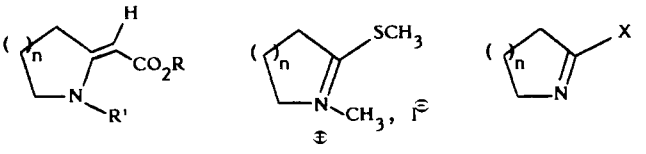
In this paper, we report a different approach to vinylogous urethanes and amides where the heterocyclic system is built at the last stage of the synthesis. This sequence is depicted in Scheme I.

The first step is a γ-monoalkylation of the dianions **6–8** with an α,ω-dihaloalkane **9** followed by a nucleophilic displacement of X (X = Br, Cl) by NaN_3, leading to the azides **13–15** that react with 1 equiv of Ph_3P in anhydrous solvents (ether or benzene) to give the vinylogous urethanes or amides **16–18**. This last step occurs via a Staudinger reaction[7] followed by an intramolecular aza-Wittig reaction.[8,9]

Results and Discussion

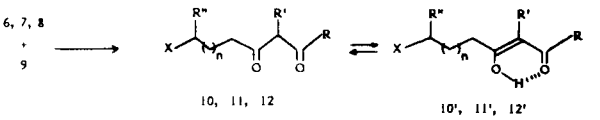
Although the γ-alkylation of dianions of β-dicarbonyl compounds has been achieved with a variety of electrophiles,[10] little is known when these electrophiles are α,ω-dihaloalkanes. The alkylation of disodioacetylacetone with dihaloalkanes has been used to synthetize bis(β-diketones).[11] The condensation of methyl acetoacetate dianion with 1,3-dibromopropane leads to a mixture of 2-carbomethoxycyclohexanone and the bis γ-alkylation

Chart I



1 2 3 : X = OMe 4 : X = SMe 5 : X = Cl

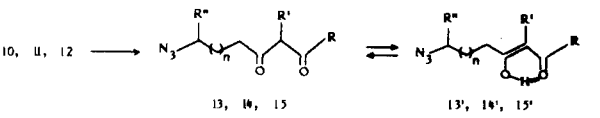
Table I. γ-Alkylation of Dianions 6–8



product	X	n	R	R′	R″	% yield[a]
10a ⇄ 10′a	Cl	1	OC_2H_5	H	H	66
10b ⇄ 10′b	Cl	2	OC_2H_5	H	H	77
10c ⇄ 10′c	Br	2	OC_2H_5	H	CH_3	58
10d ⇄ 10′d	Cl	3	OC_2H_5	H	H	68
10e ⇄ 10′e	Br	4	OC_2H_5	H	H	70
11 ⇄ 11′	Cl	2	CH_3	H	H	70
12	Cl	2	OCH_2CH_2		H	70

[a] Isolated purified products as mixtures of tautomers except for **12**.

Table II. Synthesis of Azides 13–15



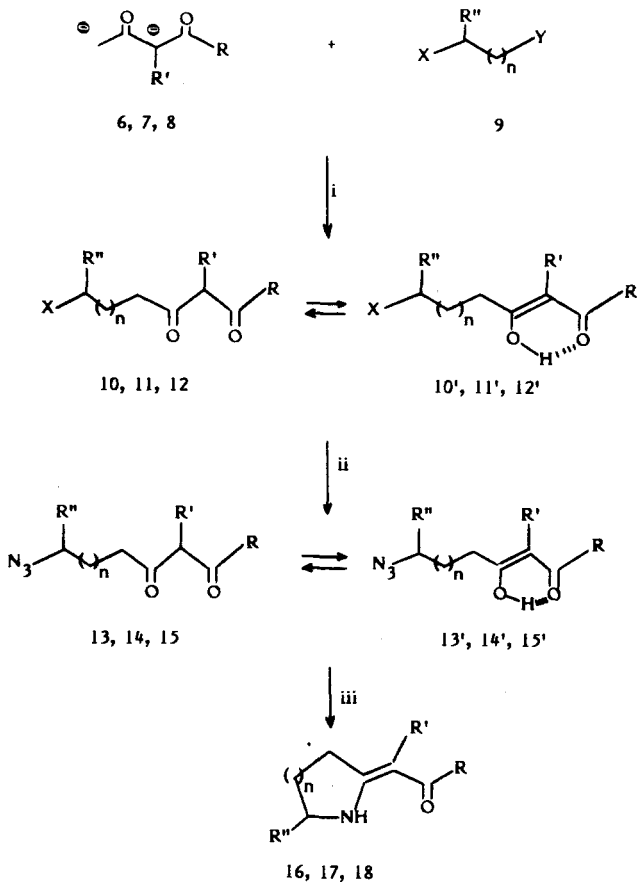
product	n	R	R′	R″	% yield[a]
13a ⇄ 13′a	1	OC_2H_5	H	H	32
13b ⇄ 13′b	2	OC_2H_5	H	H	84
13c ⇄ 13′c	2	OC_2H_5	H	CH_3	82
13d ⇄ 13′d	3	OC_2H_5	H	H	87
13e ⇄ 13′e	4	OC_2H_5	H	H	93
14a ⇄ 14′a	2	CH_3	H	H	87
15	2	OCH_2CH_2		H	95

[a] Isolated purified products as mixtures of tautomers except for **15**.

(1) Pinnick, H. W.; Chang, Y. H. *J. Org. Chem.* **1978**, *43*, 4662.
(2) Howard, A. S.; Gerrans, G. C.; Michael, J. P. *J. Org. Chem.* **1980**, *45*, 1713.
(3) Gerrans, G. C.; Howard, A. S.; Orlek, B. S. *Tetrahedron Lett.* **1975**, 4171.
(4) Roth, M.; Dubs, P.; Götschi, E.; Eschenmoser, A. *Helv. Chim. Acta* **1971**, *54*, 710.
(5) Gugelchuk, M. M.; Hart, D. J.; Tsai, Y. M. *J. Org. Chem.* **1981**, *46*, 3671 and references cited.
(6) (a) Célérier, J. P.; Deloisy, E.; Lhommet, G.; Maitte, P. *J. Org. Chem.* **1979**, *44*, 3089. (b) Célérier, J. P.; Lhommet, G.; Maitte, P. *Tetrahedron Lett.* **1981**, *22*, 963. (c) Célérier, J. P.; Richaud, M. G.; Lhommet, G. *Synthesis* **1983**, 195 and references cited. (d) Célérier, J. P.; Deloisy, E.; Kapron, P.; Lhommet, G.; Maitte, P. *Synthesis* **1981**, 130.
(7) (a) Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635. (b) Staudinger, H.; Hauser, E. *Ibid.* **1921**, *4*, 861. (c) Gololobov, Y. G.; Zhmurova, I. N.; Kasukhin, L. F. *Tetrahedron* **1981**, *37*, 437 and references cited therein.
(8) Johnson, A. W. "Ylid Chemistry"; Academic Press: New York and London, 1966; pp 222–236 and references therein. Cadogan, J. I. G. "Organophosphorus Reagents in Organic Synthesis"; Academic Press: New York and London, 1979; pp 241–249 and references therein. Pailer, M.; Haslinger, E. *Monatsh. Chem.* **1970**, *101*, 508. Leyshon, L. J.; Saunders, D. G. *J. Chem. Soc., Chem. Commun.* **1971**, 1608. Foster, S. A.; Leyshon, L. J.; Saunders, D. G. *J. Chem. Soc., Chem. Commun.* **1973**, 29. Ohler, E.; Schmidt, U. *Chem. Ber.* **1975**, *108*, 2907. Ackrell, J.; Galeazzi, E.; Muchowski, J. M.; Tökés, L. *Can. J. Chem.* **1979**, *57*, 2696 and references therein. Abel, E. W.; Mucklejohn, S. A. *Phosphorus Sulfur* **1981**, *9*, 235. Brossmer, R.; Mack, H. *Tetrahedron Lett.* **1981**, *22*, 933. Lambert, P. H.; Vaultier, M.; Carrié, R. *J. Chem. Soc., Chem. Commun.* **1982**, 1224. Sasaki, T.; Eguchi, S.; Okano, T. *J. Am. Chem. Soc.* **1983**, *105*, 5912. Hickey, D. M. B.; MacKenzie, A. R.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **1984**, 776.
(9) Kloek, J. A.; Leschinski, K. L. *J. Org. Chem.* **1978**, *43*, 1460.
(10) Harris, T. M.; Harris, C. M. *Org. React.* **1969**, *17*, 155.
(11) Hampton, K. G.; Light, R. J.; Hauser, C. R. *J. Org. Chem.* **1965**, *30*, 1413.

0022-3263/85/1950-5352$01.50/0

Scheme I[a,b]



[a] Reagents: (i) THF, −23 °C, 20 h, and then NH_4Cl at $t < 0$ °C; (ii) NaN_3, Me_2SO; (iii) Ph_3P, ether or benzene. [b] Compounds **16** and **17** for which R′ = CH_3, although resulting from a methylation of **13** and **14**, are included in this scheme for clarity.

product.[12] No ω-halo β-dicarbonyl compounds resulting from a γ-monoalkylation of the dianions were obtained. By using carefully chosen reaction and quench temperatures, one might expect to obtain the mono-γ-alkylation products. Indeed, when the dianions **6–8** were allowed to react with α,ω-dihaloalkanes **9** for 20 h at −23 °C and the reactions were then quenched at this temperature, with a cold NH_4Cl solution, the ω-halo β-dicarbonyl derivatives **10–12** were obtained in good yields (Table I), and thus the side reactions mentioned above[12] were avoided.

In the case of **12**, because of insolubility of the lithio sodio dianion, we used the soluble lithio dianion. The tautomerism equilibria **10** ⇄ **10′** and **11** ⇄ **11′** were observed in the NMR spectra in $CDCl_3$ solutions (**10**/**10′** = 9/1, **11**/**11′** = 2/8).

Azides **13–15** were easily obtained respectively from the halo derivatives **10–12** by nucleophilic substitution of the chloride (55 °C, 18 h) or the bromide (25 °C, 24 h) with sodium azide in Me_2SO in good yields (Table II).

Again, equilibria **13** ⇄ **13′** (9/1) and **14** ⇄ **14′** (2/8) were observed, however not for **15** ⇄ **15′**. The azide **13a** was isolated in a disappointing 32% yield. In fact, the NMR of the crude reaction mixture showed the formation of three compounds identified as **13a**, **19**, and **19′** (4/4/2 ratio) according to Scheme II.

The pure **13a**, **19**, and **19′** were easily separated by column chromatography. The assignment of the isomers **19** and **19′** is based on spectral features comparable to

(12) Huskin, S. N.; Weiler, L. *J. Am. Chem. Soc.* **1974**, *96*, 1082.

Scheme II

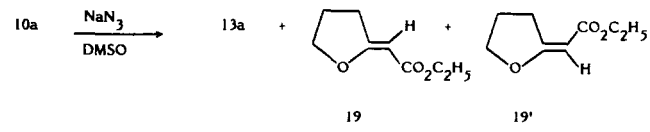
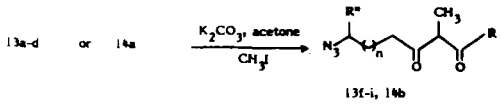


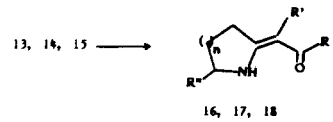
Table III. Monomethylation of 13a–d and 14a



product	n	R	R″	% yield[a]
13f	1	OCH_3	H	88
13g	2	OC_2H_5	H	94
13h	2	OC_2H_5	CH_3	98
13i	3	OC_2H_5	H	88
14b	2	CH_3	H	90[b]

[a] Isolated purified products. [b] Isolated as a mixture of the two tautomers **14b** ⇄ **14′b** (enol form) (73/27).

Table IV. Synthesis of Vinylogous Urethanes and Amides 16–18



product	n	R	R′	R″	% yield[a]
16a	1	OC_2H_5	H	H	96
16b	2	OC_2H_5	H	H	95
16c	2	OC_2H_5	H	CH_3	84
16d	3	OC_2H_5	H	H	84
16e	4	OC_2H_5	H	H	38[b]
16f	1	OCH_3	CH_3	H	84
16g	2	OC_2H_5	CH_3	H	85
16h	2	OC_2H_5	CH_3	CH_3	74
16i	3	OC_2H_5	CH_3	H	55
17a	2	CH_3	H	H	87
17b	2	CH_3	CH_3	H	87
18	2	OCH_2CH_2		H	60

[a] Isolated purified products. [b] See text.

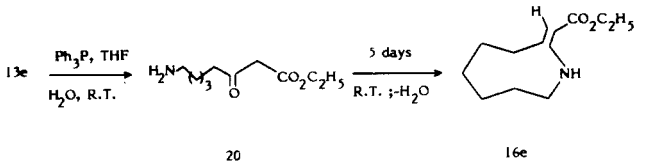
literature data found for similar systems.[13] In the 80-MHz ^1H NMR spectrum of (*Z*)-**19** the allylic protons of the tetrahydrofuran ring resonate at δ 2.79 whereas in the (*E*)-**19′** they appear at δ 3.12 due to the deshielding effect of the ester carbonyl. The shielding effect of the ring oxygen is seen in the shift of the vinyl protons of **19** (δ 4.92) as compared to **19′** (δ 5.29). **19** and **19′** are the result of an intramolecular O-alkylation of the anion of **10a** generated by sodium azide, which is a strong enough base in Me_2SO to remove reversibly a hydrogen. These intramolecular O-alkylations have some precedent in the literature.[14]

The ω-azido β-dicarbonyl derivatives **13a–d** and **14a** are readily mono-C-methylated by iodomethane in acetone with potassium carbonate as a base, leading to the azides **13f–i** and **14b**. Results are summarized in Table III.

With these ω-azido β-carbonyl compounds in hand, we next turned to the cyclization step. The treatment of **13–15** with 1 equiv of triphenylphosphine in anhydrous ether or benzene under nitrogen led quantitatively to the corresponding vinylogous urethanes and amides **16–18** via

(13) Trost, B. M.; Runge, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 7550.
(14) (a) Bartlett, P. A.; Meadows, J. D.; Ottow, E. *J. Am. Chem. Soc.* **1984**, *106*, 5304 and references cited. (b) Martel, J.; Blade-Font, A.; Marie, C.; Vivat, M.; Toromanoff, E.; Buendia, J. *Bull. Soc. Chim. Fr.* **1978**, *2*, 131. (c) Bartlett, P. A.; Jernstedt, K. K. *Tetrahedron Lett.* **1980**, 1602. (d) Lhommet, G.; Eskenazi, C.; Maitte, P. *C.R. Seances Acad. Sci., Ser. C* **1974**, *279*, c, 263.

Scheme III



an intramolecular aza-Wittig reaction. The results are summarized in Table IV.

The eight-membered vinylogous urethane **16e** could not be obtained directly by an intramolecular aza-Wittig reaction even at the temperature of boiling toluene. Nevertheless, **16e** was obtained in the following manner (Scheme III).

The azide **13e** was reduced quantitatively into the primary amine **20** via the hydrolysis of the corresponding phosphinimine.[15] **20** cyclized quantitatively, although slowly (5 days at room temperature), to give **16e**, which was isolated in the pure state by column chromatography on silica gel in a 38% yield due to partial degradation during this operation. The stereochemistry of the double bond is *Z* in all cases listed in Table IV. This results from the examination of the IR frequencies of the carbonyl groups, which are lowered by a chelation of the latter with the hydrogen beared by the nitrogen atom (1636–1665 cm^{-1} for the ester carbonyls, 1678 cm^{-1} for the lactone **18**, and 1600 and 1592 cm^{-1} for the enamino ketones **17a** and **17b**). Furthermore, the δ values for the allylic protons are in agreement with those reported in the literature.[4,6] In addition, for the vinylogous urethanes and amides where R′ = Me, the carbon of this methyl group resonates upfield ($\delta \sim 12$). This is particularly appearent for the compound **16f** for which we have prepared the *E* isomer **16′f** by another route.[16] The $\delta(^{13}C)$ values for the methyl groups are respectively 12.9 and 23.4 ppm, thus showing an important γ effect in the *Z* isomers.

To summarize, we have reported an efficient access to vinylogous urethanes and amides that may complement those existing in the literature. This sequence involving a cyclization at the ultimate step seems to have some flexibility as far as the size of the ring and the substitution are concerned. This also demonstrates the possibilities somewhat forgotten of the old Staudinger reaction followed by an aza-Wittig cyclization to build unsaturated nitrogen heterocycles and the versatility of the azido group as well.

Experimental Section

Caution! Because of their potentially explosive character, all the experiments involving azido derivatives must be carried out with the appropriate protection under a well ventilated hood.

General Methods. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Ethyl and methyl acetoacetate, acetylacetone, and α-acetylbutyrolactone were distilled prior to use. All the dihalo derivatives were dried over $CaCl_2$ and distilled prior to use. Dimethyl sulfoxyde (Me_2SO) was used as received from Aldrich. All melting points were taken with a Kofler apparatus. NMR spectra were recorded on the following spectrometers: Bruker WP 80 CW (80 MHz for ^1H) and Bruker WP 80 DS (20.115 MHz for ^{13}C; Centre de Mesures Physiques de l'Université de Rennes). They were recorded in $CDCl_3$, chemical shifts are reported in δ downfield from tetramethylsilane (Me_4Si) used as an internal standard, and coupling constants are given in Hertz (Hz). The following notations are used for multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; br s, broad singlet. Chemical shifts related to the enol forms **10′**, **11′**, **13′**, and **14′** are noted as starred values when they are available. IR spectra were determined with a Perkin-Elmer 225 spectrometer on liquid films unless otherwise indicated. The frequencies of the C=O and C=C related to the enol forms **10′**, **11′**, **13′**, and **14′** are given as starred values. High-resolution mass spectra (electron impact, 70 eV) were obtained with a Varian MAT 311 (Centre de Mesures Physiques de l'Université de Rennes). Analytical thin-layer chromatography (TLC) was performed by using silica gel 60 F 254 aluminum plates. The following abbreviations are used for eluting solvent systems: E, diethyl ether; PE, petroleum ether (bp <65 °C); E/PE (a/b), diethyl ether/petroleum ether mixture in a relative ratio a/b (volume by volume). Column chromatography was performed over Merck 60 silica gel (230–400 mesh). Unless otherwise noted, reactions were carried out under a nitrogen atmosphere with magnetic stirring in flame-dried glassware.

γ-Alkylation of the Dianions 6–8. The lithio sodio dianions of ethyl or methyl acetoacetate and acetylacetone were prepared according to ref 12. The lithio dianion of α-acetylbutyrolactone was obtained at 0 °C by using 2.1 equiv of LDA. The 0.35 M solutions of dianions were cooled to −50 °C, and then the α,ω-dihaloalkanes were introduced slowly via syringe. At the end of the addition, the temperature was allowed to reach −23 °C (0.5 h) at which time the reaction vessel was stored at this temperature for 20 h. Then, a cooled (~0 °C) saturated aqueous NH_4Cl solution (100 mL for a 0.1-mol scale reaction) was added at once to the reaction mixture maintained at −23 °C with vigorous stirring. After 15 min, the mixture was allowed to warm up to room temperature. Solvents were removed in vacuo and the residue extracted three times with ether. The ether extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by distillation or column chromatography.

Ethyl 6-Chloro-3-oxohexanoate (10a). From 13.0 g (12.75 mL, 100 mmol) of ethyl acetoacetate and 14.3 g of 1-bromo-2-chloroethane was obtained 19.1 g of **10a**: bp 92–93 °C (0.1 torr) (lit.[14d] bp 100 °C (0.1 torr)); mp 24–25 °C (hexane); TLC R_f 0.67 (E/PE 1/1); IR 1736, 1708, 1638*, 1620* cm^{-1}; ^1H NMR δ 1.35 (3 H, t, J = 7.0 Hz), 1.90–2.30 (2 H, m), 2.35–2.60* (0.4 H, m), 2.81 (1.6 H, t, J = 6.7 Hz), 3.50 (1.6 H, s), 3.62 (2 H, t, J = 6.2 Hz), 4.24 (2 H, q, J = 7.0 Hz), 5.06* (0.2 H, s), 12.14* (0.2 H, s); ^{13}C NMr δ 14.2, 26.3, 39.7, 44.2, 49.5, 61.5, 167.2, 201.9. Anal. Calcd for $C_8H_{13}O_3Cl$: C, 49.87; H, 6.75; O, 24.94. Found: C, 49.70; H, 6.75; O, 25.06.

Ethyl 7-Chloro-3-oxoheptanoate (10b). From 13.0 g (12.75 mL, 100 mmol) of ethyl acetoacetate and 15.7 g (10.7 mL, 100 mmol) of 1-bromo-3-chloropropane was obtained 15.9 g of **10b**: bp 89–90 °C (0.05 torr); IR, 1740, 1709, 1640*, 1625* cm^{-1}; ^1H NMR δ 1.32 (3 H, t, J = 7.0 Hz), 1.62–2.07 (4 H, m), 2.07–2.45* (0.2 H, m), 2.50–2.85 (1.8 H, m), 3.40–3.72 (2 H, m), 3.47 (1.8 H, s), 4.22 (2 H, q, J = 7.0 Hz), 5.02* (0.1 H, s), 12.12* (0.1 H, s); ^{13}C NMR δ 14.1, 20.8, 23.6*, 31.8, 34.2*, 42.0, 44.6, 49.3, 60.1*, 61.4, 89.6*, 167.3, 172.9*, 178.1*, 202.3. Anal. Calcd for $C_9H_{15}O_3Cl$: C, 52.30; H, 7.26; O, 23.24. Found: C, 52.53; H, 7.30; O, 23.17.

Ethyl 7-Bromo-3-oxooctanoate (10c). From 13.0 g (12.75 mL, 100 mmol) of ethyl acetoacetate and 21.6 g (12.0 mL, 100 mmol) of 1,3-dibromobutane was obtained 14.6 g of **10c**: bp 116–118 °C (0.05 torr); IR 1735, 1709, 1619* (br) cm^{-1}; ^1H NMR δ 1.32 (3 H, t, J = 7.0 Hz), 1.75 (3 H, d, J = 6.6 Hz), 1.60–2.05 (4 H, m), 2.05–2.45* (0.2 H, m), 2.47–2.57 (1.8 H, m), 3.46 (1.8 H, s), 3.92–4.35 (1 H, m), 4.22 (2 H, q, J = 7.0 Hz), 5.02* (0.1 H, s), 12.12* (0.1 H, s); ^{13}C NMR δ 14.1, 21.7, 24.5*, 26.4, 34.2*, 40.1, 41.1*, 42.0, 49.3, 50.1*, 50.9, 60.0*, 61.3, 89.4*, 167.2, 178.0*, 202.3; mass spectrum, exact mass calcd for $C_{10}H_{17}BrO_3$ m/e 264.036, found m/e 264.034.

Ethyl 8-Chloro-3-oxooctanoate (10d). From 2.6 g (2.55 mL, 20 mmol) of ethyl acetoacetate and 3.4 g (2.30 mL, 20 mmol) of 1-bromo-4-chlorobutane was obtained 3.0 g of **10d**: bp 97–98 °C (0.05 torr); IR 1742, 1707, 1640*, 1620* cm^{-1}; ^1H NMR δ 1.32 (3 H, t, J = 7.0 Hz), 1.25–2.00 (6 H, m), 2.05–2.45* (0.3 H, m), 2.75 (1.7 H, t, J = 6.5 Hz), 3.46 (1.7 H, s), 3.56 (2 H, t, J = 6.3 Hz), 4.21 (2 H, q, J = 7.0 Hz), 5.00* (0.15 H, s), 12.12* (0.15 H, s); ^{13}C NMR δ 14.2, 22.7, 25.6*, 26.4, 32.5, 34.9*, 42.7, 44.8, 49.4, 60.0*, 61.3, 89.3*, 167.4, 172.9*, 178.6*, 202.6. Anal. Calcd for $C_{10}H_{17}ClO_3$: C, 54.42; H, 7.71; O, 21.77. Found: C, 55.06; H, 7.87; O, 21.61.

Ethyl 9-Bromo-3-oxononanoate (10e). From 1.30 g (1.28 mL, 10 mmol) of ethyl acetoacetate and 2.30 g (1.36 g, 10 mmol) of 1,5-dibromopentane was obtained 1.97 g of **10e**: bp 135–136 °C

(15) Vaultier, M.; Knouzi, N.; Carrié, R. *Tetrahedron Lett.* **1983**, 763.
(16) Knouzi, N. Thèse de 3ème Cycle, University of Rennes, 1983.

(0.05 torr); mp 12–13 °C (E/PE 1/1); IR 1738, 1712, 1642*, 1624* cm^{-1}; ^1H NMR δ 1.31 (3 H, t, J = 7.0 Hz), 1.25–2.10 (8 H, m), 2.15–2.40* (0.2 H, m), 2.60 (1.8 H, t, J = 6.8 Hz), 3.42 (2 H, t, J = 6.5 Hz), 3.45 (1.8 H, s), 4.20 (2 H, q, J = 7.0 Hz), 5.00* (0.1 H, s), 12.11* (0.1 H, s); ^{13}C NMR δ 14.2, 23.2, 26.1*, 27.9, 28.1, 32.6, 33.7, 34.9*, 42.7, 49.4, 59.9*, 61.3, 89.2*, 167.3, 172.9*, 178.8*, 202.7. Anal. Calcd for $C_{11}H_{19}BrO_3$: C, 47.31; H, 6.81; O, 17.20. Found: C, 47.46; H, 7.03; O, 17.37.

8-Chloro-4-oxo-2-octanone (11). From 10.01 g (10.3 mL, 100 mmol) of acetylacetone and 15.74 g (10.7 mL, 100 mmol) of 1-bromo-3-chloropropane was obtained 13.57 g of **11** after column chromatography (E/PE 1/1): bp 83–85 °C (0.05 torr); TLC R_f 0.66 (E/PE 1/1); IR 1720, 1700, 1610* (br) cm^{-1}; ^1H NMR δ 1.65–2.02 (4 H, m), 2.10* (2.4 H, s), 2.29 (0.6 H, s), 2.20–2.50* (1.6 H, m), 2.55–2.80 (0.4 H, m), 3.45–3.77 (2 H, m), 3.64 (0.4 H, s), 5.54* (0.8 H, s), 15.37* (0.8 H, br s); ^{13}C NMR δ 20.8, 22.9*, 24.8*, 30.9, 31.8, 32.0*, 37.4*, 42.8, 44.6*, 57.8, 99.9*, 191.3*, 193.8*, 202.1. Anal. Calcd for $C_8H_{13}ClO_2$: C, 54.39; H, 7.37; O, 18.13. Found: C, 54.46; H, 7.52; O, 18.14.

2-[5-Chloropentanoyl]butyrolactone (12). From 4.93 g (4.15 mL, 38.5 mmol) of α-acetylbutyrolactone and 6.06 g (3.81 mL, 38.5 mmol) of 1-bromo-3-chloropropane was obtained 5.55 g of **12** after column chromatography (Et_2O/MeOH 99/1): bp 110–115 °C (0.01 torr); TLC R_f 0.56 (Et_2O/MeOH 99/1); IR 1760, 1713 cm^{-1}; ^1H NMR δ 1.67–2.05 (4 H, m), 2.17–3.12 (4 H, m), 3.47–3.72 (2 H, m), 3.76 (1 H, dd, J = 6.9 and 9.1 Hz), 4.22–4.57 (2 H, m); ^{13}C NMR δ 20.7, 24.1, 31.8, 41.3, 44.7, 42.3, 67.6, 173.1, 202.5. Anal. Calcd for $C_9H_{13}ClO_3$: C, 52.81; H, 6.36; O, 23.47. Found: C, 52.82; H, 6.45; O, 23.29.

Nucleophilic Displacement of Halides by Sodium Azide. General Procedure. To a solution of 10 mmol of the halo derivatives **10a–e**, **11**, and **12** in 20 mL of Me_2SO were added with stirring 975 mg (15 mmol, 1.5 equiv) of powdered NaN_3 and a catalytic amount of sodium iodide (~50 mg). Then, the suspension was heated (50–55 °C, oil bath) with stirring for 12–18 h. After cooling, water (40 mL) was added and the mixture extracted with ether (4 × 20 mL). The ether extracts were washed with brine (3 × 10 mL) and dried over Na_2SO_4. The solvent was removed in vacuo and the crude oil thus obtained purified either by bulb to bulb transfer (Kügelrohr) or by column chromatography.

Ethyl 6-Azido-3-oxohexanoate (13a). From 6.72 g (34.9 mmol) of **10a** was obtained by column chromatography (E/PE 1/1) 2.20 g of **13a**: bp 102–105 °C (0.02 torr); TLC R_f 0.55 (E/EP 1/1); IR 2088, 1734, 1709, 1638*, 1622* cm^{-1}; ^1H NMR δ 1.35 (3 H, t, J = 7.0 Hz), 1.75–2.10 (2 H, m), 2.15–2.47* (0.2 H, m), 2.76 (1.8 H, t, J = 6.8 Hz), 3.39 (2 H, t, J = 6.5 Hz), 3.50 (1.8 H, s), 4.25 (2 H, q, J = 7.0 Hz), 5.05* (0.1 H, s), 12.11* (0.1 Hz, s); ^{13}C NMR δ 14.2, 18.3*, 22.9, 32.1*, 39.6, 49.4, 50.7, 60.2*, 61.5, 89.9*, 167.2, 201.9. Anal. Calcd for $C_8H_{13}N_3O_3$: C, 48.24; H, 6.53; N, 21.11. Found: C, 48.53; H, 6.67; N, 20.87.

19: 545 mg, yield 10%; R_f 0.22 (E/PE 1/1); IR 1704, 1643 cm^{-1}; ^1H NMR δ 1.26 (3 H, t, J = 7.0 Hz), 1.85–2.32 (2 H, m), 2.60–2.92 (2 H, m), 4.16 (2 H, q, J = 7.0 Hz), 4.87 (1 H, t, J = 1, 2 Hz); ^{13}C NMR δ 14.5, 23.4, 32.2, 59.1, 74.4, 88.2, 166.0, 172.4; mass spectrum, exact mass calcd for $C_8H_{12}O_3$ m/e 156.079, found, m/e 156.079.

19′: 1.64 g, yield 30%; R_f 0.65 (E/EP 1/1); IR 1696, 1639 cm^{-1}; ^1H NMR δ 1.29 (3 H, t, J = 7.1 Hz), 1.90–2.35 (2 H, m), 3.12 (2 H, dt, J = 7.7 and 1.7 Hz), 4.14 (2 H, q, J = 7.1), 4.24 (2 H, J = 6.9 Hz), 5.29 (1 H, t, J = 1.7 Hz); ^{13}C NMR δ 14.5, 23.9, 30.3, 59.2, 71.9, 89.7, 168.7, 176.8. Anal. Calcd for $C_8H_{12}O_3$: C, 61.54; H, 7.69. Found: C, 61.20; H, 7.79.

Ethyl 7-Azido-3-oxoheptanoate (13b). From 15.90 g (77 mmol) of **8b** was obtained 13.75 g of **13b** after Kügelrohr distillation: bp 90–105 °C (oven temperature) (0.1 torr); TLC R_f 0.59 (E/PE 1/1); IR 2087, 1740, 1714, 1642*, 1622* cm^{-1}; ^1H NMR δ 1.31 (3 H, t, J = 7.0 Hz), 1.47–1.87 (4 H, m), 2.07–2.35* (0.2 H, m), 2.50–2.80 (1.8 H, m), 3.20–3.52 (2 H, m), 3.45 (1.8 H, s), 4.20 (2 H, q, J = 7.0 Hz), 5.00* (0.1 H, s), 12.09* (0.1 H, s); ^{13}C NMR δ 14.1, 20.7, 28.2, 42.2, 49.4, 51.3, 61.4, 167.3, 202.2; mass spectrum, exact mass calcd for $C_9H_{15}NO_3$ $[M - N_2]^{+\cdot}$ m/e 185.105, found m/e 185.107.

Ethyl 7-Azido-3-oxooctanoate (13c). From 12.25 g (46.2 mmol) of **8c** was obtained 8.60 g of **13c** after column chromatography (E/PE 1/3): bp 55 °C (oven temperature) (0.01 torr); TLC R_f 0.56 (E/PE 1/3); IR 2092, 1735, 1711, 1640*, 1620* cm^{-1}; ^1H NMR δ 1.32 (3 H, t, J = 7.1 Hz), 1.25–2.00 (4 H, m), 1.29 (3 H, d, J = 6.5 Hz), 2.05–2.35* (0.2 H, m), 2.62 (1.8 H, t, J = 6.7 Hz), 3.45 (1.8 H, s), 3.50 (1 H, sext, J = 6.5 and 6.7 Hz), 4.21 (2 H, q, J = 7.1 Hz), 5.00* (0.1 H, s), 12.36* (0.1 H, s); ^{13}C NMR δ 14.1, 19.3, 20.0, 22.9*, 34.7*, 35.4, 42.4, 49.3, 57.8, 60.0*, 61.3, 89.5*, 167.3, 172.9*, 178.2*, 202.4. Anal. Calcd for $C_{10}H_{17}N_3O_3$: C, 52.86; H, 7.49; N, 18.50. Found: C, 52.78; H, 7.80; N, 18.53.

Ethyl 8-Azido-3-oxooctanoate (13d). From 7.25 g (34.4 mmol) of **10d** was obtained 6.80 g of **13d** after column chromatography (E/PE 1/3): TLC R_f 0.65 (E/PE 1/1); IR 2088, 1739, 1708, 1642* (br) cm^{-1}; ^1H NMR δ 1.31 (3 H, t, J = 7.1 Hz), 1.30–1.95 (6 H, m), 2.17* (0.2 H, t, J = 6.5 Hz), 2.61 (1.8 H, t, J = 6.5 Hz), 3.31 (2 H, t, J = 6.3 Hz), 3.45 (1.8 H, s), 4.21 (2 H, q, J = 7.1 Hz), 5.00* (0.1 H, s), 12.12* (0.1 H, br s); ^{13}C NMR δ 14.2, 14.3*, 23.0, 25.9*, 26.2, 28.8, 34.9*, 42.7, 49.4, 51.4, 60.0*, 61.3, 89.4*, 167.4, 173.0*, 178.6*, 202.7; mass spectrum, exact mass calcd for $C_8H_{12}NO_2$ $[M - N_2 - EtO]^+$ m/e 154.087, found m/e 154.087.

Ethyl 9-Azido-3-oxononanoate (13e). From 14.2 g (50.1 mmol) of **10e** was obtained 14.20 g of **13e** after Kügelrohr distillation: bp 100–105 °C (oven temperature) (0.05 torr); IR 2087, 1743, 1709, 1640, 1617 cm^{-1}; ^1H NMR δ 1.32 (3 H, t, J = 7.0 Hz), 1.27–1.92 (8 H, m), 2.17* (0.2 H, t, J = 6.8 Hz), 2.61 (1.8 H, t, J = 6.8 Hz), 3.31 (2 H, t, J = 6.4 Hz), 3.45 (1.8 H, s), 4.21 (2 H, q, J = 7.0 Hz), 5.01* (0.1 H, s), 12.12* (0.1 H, br s); ^{13}C NMR δ 14.2, 23.3, 26.2*, 26.6, 28.6, 28.8, 34.9*, 42.7, 49.4, 51.4, 60.0*, 61.3, 89.2*, 167.4, 173.0*, 178.9*, 202.8. Anal. Calcd for $C_{11}H_{19}N_3O_3$: C, 54.77; H, 7.88; N, 17.43. Found: C, 54.44; H, 7.99; N, 17.18.

8-Azido-4-oxo-2-octanone (14a). From 2.65 g (15.0 mmol) of **11** was obtained 2.40 g of **14a** (Kügelrohr distillation): bp 68–83 °C (oven temperature); IR 2089, 1722, 1695*, 1604* (br) cm^{-1}; ^1H NMR δ 1.55–2.00 (4 H, m), 2.10* (2.4 H, s), 2.29 (0.6 H, s), 2.20–2.50* (1.6 H, m), 2.55–2.77 (0.4 H, m), 3.20–3.52 (2 H, m), 3.62 (0.4 H, s), 5.52* (0.8 H, s), 15.42* (0.8 H, br s); ^{13}C NMR δ 20.6, 22.7*, 24.8*, 28.2, 28.4*, 37.7*, 30.8, 43.0, 44.6, 51.2*, 57.8, 99.9*, 191.3*, 193.8*, 202.1, 203.6; mass spectrum, exact mass calcd for $C_6H_{11}N_3O$ $[M - CH_2CO]^{+\cdot}$ m/e 141.090, found m/e 141.093.

2-(5-Azidopentanoyl)butyrolactone (15). From 2.90 g of **12** (14.2 mmol) was obtained 1.15 g of **15** (column chromatography E/MeOH 99/1): bp 100–105 °C (0.01 torr); TLC R_f 0.71 (E/MeOH 99/1); IR 2081, 1762, 1707 cm^{-1}; ^1H NMR δ 1.37–2.00 (4 H, m), 2.07–3.12 (4 H, m), 3.20–3.55 (2 H, m), 3.77 (1 H, dd, J = 9.2 and 7.0 Hz), 4.22–4.62 (2 H, m); ^{13}C NMR δ 20.5, 24.1, 28.2, 41.6, 51.2, 52.3, 67.6, 173.1, 202.4. Anal. Calcd for $C_9H_{13}N_3O_3$: C, 51.18; H, 6.16. Found: C, 51.35; H, 6.12.

Alkylation of ω-Azido β-Dicarbonyl Derivatives 13a–d and 14a. General Procedure. To a solution of 10 mmol of **13a–d** and **14a** in 50 mL of acetone were added 2.76 g of anhydrous K_2CO_3 (20 mmol) and 1.42 g (0.623 mL, 10 mmol) of freshly distilled iodomethane. The reaction mixture was stirred at room temperature for 20 h. After filtration and removal of the solvant under vacuum, the oily residue was purified by Kügelrohr distillation (oven temperature given).

Methyl 6-Azido-2-methyl-3-oxohexanoate (13f). A 3.04-g portion (16.4 mmol) of **13a** gave 2.88 g of **13f**: bp 65–85 °C (0.5 torr); IR 2087, 1747, 1709 cm^{-1}; ^1H NMR δ 1.40 (3 H, d, J = 7.1 Hz), 1.72–2.17 (2 H, m), 2.57–2.87 (2 H, m), 3.36 (2 H, t, J = 6.6 Hz), 3.60 (1 H, q, J = 7.1 Hz), 3.77 (3 H, s); ^{13}C NMR δ 12.8, 23.0, 38.0, 50.7, 52.4, 52.8, 171.0, 204.9. Anal. Calcd for $C_8H_{13}N_3O_3$: C, 48.24; H, 6.53; N, 21.11. Found: C, 48.21; H, 6.65; N, 20.87.

Ethyl 7-Azido-2-methyl-3-oxoheptanoate (13g). A 2.20-g portion (10.32 mmol) of **13b** gave 2.20 g of **13g**: bp 85–95 °C (0.5 torr); IR 2088, 1737, 1709 cm^{-1}; ^1H NMR δ 1.32 (3 H, t, J = 7.0 Hz), 1.37 (3 H, d, J = 7.1 Hz), 1.40–1.95 (4 H, m), 2.50–2.82 (2 H, m), 3.17–3.50 (2 H, m), 3.57 (1 H, q, J = 7.1 Hz), 4.22 (2 H, q, J = 7.0 Hz); ^{13}C NMR δ 12.7, 14.2, 20.8, 28.3, 40.7, 51.3, 52.9, 61.4, 170,7, 205.3. Anal. Calcd for $C_{10}H_{17}N_3O_3$: C, 52.86; H, 7.49; N, 18.50. Found: C, 52.60; H, 7.53; N, 17.92.

Ethyl 7-Azido-2-methyl-3-oxooctanoate (13h). A 0.70-g portion (3.08 mmol) of **13c** gave 0.73 g of **13h**: bp 57–75 °C (0.01 torr); TLC R_f 0.65 (E.PE 1/1); IR 2090, 1735, 1707 cm^{-1}; ^1H NMR δ 1.30 (3 H, d, J = 6.5 Hz), 1.32 (3 H, t, J = 7.0 Hz), 1.36 (3 H, d, J = 7.0 Hz), 1.12–2.00 (4 H, m), 2.47–2.80 (2 H, m), 3.25–3.65 (1 H, m), 3.55 (1 H, q, J = 7.0 Hz), 4.21 (2 H, q, J = 7.0 Hz); ^{13}C NMR δ 12.7, 14.2, 19.4, 20.2, 35.5, 40.9, 52.9, 57.9, 61.3, 170.7, 205.4; mass spectrum, exact mass calcd for $C_{11}H_{18}O_3$ $[M - NH_3]^{+\cdot}$ m/e 198.126, found m/e 198.125.

Ethyl 8-Azido-2-methyl-3-oxooctanoate (13i). A 1.50-g portion (6.6 mmol) of **13d** gave 1.40 g of **13i**: TLC R_f 0.63 (E/PE 1/1); IR 2088, 1735, 1709 cm^{-1}; ^1H NMR δ 1.12–1.92 (6 H, m), 1.32 (3 H, t, J = 7.0 Hz), 1.37 (3 H, d, J = 7.0 Hz), 2.45–2.75 (2 H, m), 3.15–3.47 (2 H, m), 3.54 (1 H, q, J = 7.0 Hz), 4.21 (2 H, q, J = 7.0 Hz); mass spectrum, exact mass calcd for $C_9H_{14}N_3O_2$ $[M - EtO]^+$ m/e 196.109, found m/e 196.109.

8-Azido-3-methyl-4-oxo-2-octanone (14b). A 2.75-g portion (15.0 mmol) of **14a** gave 2.6 g of **14b**: bp 90–94 °C (0.1 torr); IR 2090, 1719, 1694, 1590* (br) cm^{-1}; ^1H NMR [ratio **14b**/**14'b** (enol form) 7/3] δ 1.37 (2.1 H, d, J = 7.0 Hz), 1.50–1.95 (4 H, m), 1.91* (0.9 H, s), 2.17* (0.9 H, s), 2.24 (2.1 H, s), 2.37–2.75 (2 H, m), 3.20–3.52 (2 H, m), 3.75 (0.7 H, q, J = 7.0 Hz), 16.50* (0.3 H, br s); ^{13}C NMR δ 12.5*, 12.7, 20.7, 22.3*, 23.2*, 28.3, 28.6, 35.3*, 41.0, 48.1*, 51.3, 61.2, 61.6*, 104.6*, 190.0*, 193.1*, 205.2, 206.7. Anal. Calcd for $C_9H_{15}N_3O_2$: C, 54.82; H, 7.61; N, 21.32. Found: C, 54.60; H, 7.78; N, 21.23.

Synthesis of Vinylogous Urethanes and Amides 16–18. General Procedure. To a solution of 10 mmol of the azides in 20 mL of anhydrous ether (or benzene for **13d** and **13i**) was added 2.62 g (10 mmol) of triphenylphosphine with stirring until all the phosphine was dissolved. Nitrogen evolution started after a few seconds. The reaction mixture was kept at room temperature for 24 h (or boiling for 3 h in the cases of **13d** and **13i**). Then, solvents were removed in vacuo and the residue triturated with 40 mL of a 1/1 mixture of ether and petroleum ether. Triphenylphosphine oxide was collected by filtration, and the crystals were thoroughly washed with cold ether. After removal of the solvents, the products were purified by Kügelrohr distillation (oven temperature) or column chromatography.

Ethyl 2-(2-Pyrrolidinylidene)acetate (16a). A 597-mg portion (3.0 mmol) of **13a** gave 447 mg of 16a: bp 75–85 °C (0.5 torr); mp 62–63 °C (hexane, lit.[6a] mp 62–63 °C). Anal. Calcd for $C_8H_{13}NO_2$: C, 61.94; H, 8.35; N, 9.03. Found: C, 61.90; H, 8.36; N, 9.21.

Ethyl 2-(2-Piperidinylidene)acetate (16b). From 1.93 g (9 mmol of **13b**) was obtained 1.45 g of **16b** (Kügelrohr): bp 75–90 °C (0.5 torr); (lit.[6a] bp 92 °C (0.1 torr)); ^{13}C NMR δ 14.8, 20.1, 23.0, 29.2, 41.3, 58.2, 80.6, 162.8, 170.8; mass spectrum, exact mass calcd for $C_9H_{15}NO_2$ m/e 169.110, found m/e 169.110.

Ethyl 2-(6-Methyl-2-piperidinylidene)acetate (16c). A 1.2-g portion (5.0 mmol) of **13c** gave 0.85 g of **16c** (Kügelrohr): bp 75–85 °C (0.05 torr); TLC R_f 0.65 (E/PE 1/1); IR 3260, 1644, 1600 cm^{-1}; ^1H NMR δ 1.24 (3 H, d, J = 6.4 Hz), 1.26 (3 H, t, J = 7.0 Hz), 1.15–2.10 (4 H, m), 2.17–2.50 (2 H, m), 3.17–3.67 (1 H, m), 4.07 (2 H, q, J = 7.0 Hz), 4.35 (1 H, s), 8.65 (1 H, br s); ^{13}C NMR δ 14.8, 19.8, 23.1, 29.0, 31.4, 47.6, 58.1, 80.4, 162.6, 170.8; mass spectrum, exact mass calcd for $C_{10}H_{17}NO_2$ m/e 183.126, found m/e 183.126.

Ethyl 2-(2-Azepinylidene)acetate (16d). A 2.27-g portion (10 mmol) of **13d** gave 1.40 g of **16d** (Kügelrohr): bp 85–87 °C (0.05 torr); mp 54–55 °C (petroleum ether, lit.[6a] mp 49 °C (methanol). Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.49; H, 9.39; N, 7.59.

Ethyl 2-(2-Azocinylidene)acetate (16e). A 1.04-g portion (4.3 mmol) of **13e** was dissolved in 20 mL of anhydrous THF. Then, 1.13 g of Ph_3P and 155 μL of H_2O (8.6 mmol) were added. The reaction mixture was kept at room temperature for 5 days. The solvent was removed under vacuum and the residue chromatographed (elution E/PE 1/1) to give, after Kügelrohr distillation of the pure fractions, 0.325 g of **16e**: bp 95–105 °C (0.01 torr); TLC R_f 0.69 (E/PE 1/1); IR 3258, 3160, 1640, 1597 cm^{-1}; ^1H NMR δ 1.27 (3 H, t, J = 7.0 Hz), 1.25–2.07 (8 H, m), 2.20–2.50 (2 H, m), 3.20–3.60 (2 H, m), 4.10 (2 H, q, J = 7.0 Hz), 4.42 (1 H, s), 8.82 (1 H, br s); mass spectrum, exact mass calcd for $C_{11}H_{19}NO_2$ m/e 197.142, found m/e 197.142; picrate mp 109–110 °C (EtOH). Anal. Calcd for $C_{17}H_{22}N_4O_9$: C, 47.89; H, 5.16; N, 13.15. Found: C, 48.29; H, 5.23; N, 13.07.

Methyl 2-(2-Pyrrolidinylidene)propanoate (16f). A 2.00-g portion (10.0 mmol) of **13f** gave 1.30 g of **16f** (Kügelrohr): bp 65–90 °C (0.1 torr); mp 54–55 °C (petroleum ether); IR (Nujol) 3335, 1665, 1595 cm^{-1}; ^1H NMR δ 1.77 (3 H, s), 1.80–2.25 (2 H, m), 2.65 (2 H, t, J = 7.5 Hz), 3.54 (2 H, t, J = 6.8), 3.70 (3 H, s), 8.15 (1 H, br s); ^{13}C NMR δ 12.9, 22.2, 31.3, 47.3, 50.3, 83.3, 164.2, 171.2; mass spectrum, exact mass calcd for $C_8H_{13}NO_2$ m/e 155.095, found m/e 155.095.

Ethyl 2-(2-Piperidinylidene)propanoate (16g). A 2.15-g portion (9.5 mmol) of **13g** gave 1.46 g of **16g**: bp 90–92 °C (0.5 torr); TLC R_f 0.62 (E/PE 1/1); IR 3229, 3146, 1636, 1592 cm^{-1}; ^1H NMR δ 1.32 (3 H, t, J = 7.0), 1.77 (3 H, s), 1.62–2.00 (4 H, m), 2.32–2.62 (2 H, m), 3.20–3.50 (2 H, m), 3.65 (2 H, q, J = 7.0 Hz), 9.55 (1 H, br s); ^{13}C NMR δ 11.4, 14.8, 20.5, 22.6, 26.7, 41.7, 58.6, 84.9, 160.0, 171.2. Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.57; H, 9.29; N, 7.65. Found: C, 65.37; H, 9.26; N, 7.47.

Ethyl 2-(6-Methyl-2-piperidinylidene)propanoate (16h). A 1.14-g portion (4.47 mmol) of **13h** gave 0.7 g of **16h** (Kügelrohr): bp 83–85 °C (0.05 torr); TLC R_f 0.67 (E/PE 1/1); IR 3230, 3140, 1636, 1597 cm^{-1}; ^1H NMR δ 1.25 (3 H, d, J = 6.3 Hz), 1.30 (3 H, t, J = 7.0 Hz), 1.25–2.15 (4 H, m), 1.76 (3 H, s), 2.20–2.62 (2 H, m), 3.15–3.70 (1 H, m), 4.12 (2 H, q, J = 7.0 Hz), 9.50 (1 H, br s); ^{13}C NMR δ 11.5, 14.8, 20.0, 23.3, 26.4, 30.8, 47.8, 58.5, 84.7, 159.9, 171.1; mass spectrum, exact mass calcd for $C_{11}H_{19}NO_2$ m/e 197.142, found m/e 197.140.

Ethyl 2-(2-Azepinylidene)propanoate (16i). A 0.93-g portion (3.86 mmol) of **13i** gave 0.45 g of **16i** (Kügelrohr): bp 95–100 °C (0.05 torr); mp 31–32 °C (hexane); TLC R_f 0.63 (E/PE 1/1); IR (Nujol) 3245, 3154, 1641, 1592 cm^{-1}; ^1H NMR δ 1.30 (3 H, t, J = 7.0 Hz), 1.47–1.90 (6 H, m), 1.85 (3 H, s), 2.40–2.70 (2 H, m), 3.17–3.50 (2 H, m), 4.14 (2 H, q, J = 7.0 Hz), 9.55 (1 H, br s). Anal. Calcd for $C_{11}H_{19}NO_2$: C, 67.01; H, 9.64; N, 7.11. Found: C, 67.06; H, 9.83; N, 7.00.

1-(2-Piperidinylidene)-2-propanone (17a). A 0.915-g portion (5.0 mmol) of **14a** gave 0.607 g of **17a** (Kügelrohr): bp 95–97 °C (0.1 torr); TLC R_f 0.33 (E/PE 1/1); IR 3385, 3205, 1600, 1555 cm^{-1}; ^1H NMR δ 1.55–2.07 (4 H, m), 2.02 (3 H, s), 2.27–2.57 (2 H, m), 3.25–3.55 (2 H, m), 4.90 (1 H, s), 11.10 (1 H, br s); ^{13}C NMR δ 19.5, 22.4, 28.5, 28.6, 41.0, 93.6, 164.1, 194.1. Anal. Calcd for $C_8H_{13}NO$: C, 67.78; H, 9.35; N, 10.33. Found: C, 67.76; H, 9.35; N, 9.96.

2-(2-Piperidinylidene)-3-butanone (17b). A 1.17-g portion of **17b** (Kügelrohr) was obtained from 1.72 g (8.7 mmol) of **14b**: bp 75–85 °C (0.05 torr); mp 65–66 °C (hexane); IR 1592, 1564 cm^{-1}; ^1H NMR δ 1.67–2.05 (4 H, m), 1.92 (3 H, s), 2.12 (3 H, s), 2.30–2.62 (2 H, m), 3.22–3.55 (2 H, m), 12.32 (1 H, br s); ^{13}C NMR δ 13.4, 20.0, 21.9, 26.6, 27.9, 41.3, 96.7, 162.5, 193.5; mass spectrum, exact mass calcd for $C_9H_{15}NO$, m/e 153.115, found m/e 153.115.

2-(2-Piperidinylidene)butyrolactone (18). A 1.16-g portion (5.48 mmol) of **15** gave, after two recrystallizations from hexane, 0.55 g of **18**: mp 76–77 °C; IR (Nujol) 3293, 1678, 1598 cm^{-1}; ^1H NMR δ 1.62–2.05 (4 H, m), 2.20–2.57 (2 H, m), 2.77 (2 H, t, J = 7.9 Hz), 3.17–3.55 (2 H, m), 4.27 (2 H, t, J = 7.9 Hz), 8.32 (1 H, br s); ^{13}C NMR δ 19.7, 22.5, 25.8, 27.1, 41.6, 65.4, 82.8, 157.7, 174.3. Anal. Calcd for $C_9H_{13}NO_2$: C, 67.18; H, 6.66; N, 8.14. Found: C, 67.46; H, 6.77; N, 8.26.

Registry No. **10a**, 54362-87-7; **10'a**, 99054-00-9; **10b**, 99054-01-0; **10'b**, 99054-02-1; **10c**, 99054-03-2; **10'c**, 99054-04-3; **10d**, 99054-05-4; **10'd**, 99054-06-5; **10e**, 99054-07-6; **10'e**, 99054-08-7; **11**, 22977-45-3; **11'**, 99054-09-8; **12**, 99054-10-1; **13a**, 99054-11-2; **13'a**, 99054-12-3; **13b**, 99054-13-4; **13'b**, 99054-14-5; **13c**, 99054-15-6; **13'c**, 99054-16-7; **13d**, 99054-17-8; **13'd**, 99054-18-9; **13e**, 99054-19-0; **13'e**, 99054-20-3; **13f**, 99054-24-7; **13g**, 99054-25-8; **13h**, 99054-26-9; **13i**, 99054-27-0; **14a**, 99054-21-4; **14'a**, 99054-22-5; **14b**, 99054-28-1; **14'b**, 99054-29-2; **15**, 99054-23-6; (*Z*)-**16a**, 35150-22-2; (*Z*)-**16b**, 25654-24-4; (*Z*)-**16c**, 99054-30-5; (*Z*)-**16d**, 70912-51-5; (*Z*)-**16e**, 99054-31-6; (*E*)-**16f**, 99054-32-7; (*Z*)-**16g**, 96333-47-0; (*Z*)-**16h**, 99054-33-8; (*Z*)-**16i**, 96333-52-7; (*Z*)-**17a**, 25654-25-5; (*Z*)-**17b**, 99054-34-9; (*Z*)-**18**, 99054-35-0; (*Z*)-**19**, 99054-36-1; (*E*)-**19'**, 99054-37-2; $EtO_2CCHCOCH_2^{2-}\cdot Li^+\cdot Na^+$, 40902-62-3; $CH_3COCHCOCH_2^{2-}\cdot Li^+\cdot Na^+$, 56580-16-6; $\overline{CH_2CH_2OCOCCO}$-$CH_2^{2-}\cdot Li^+\cdot Na^+$, 99053-99-3; $Br(CH_2)_2Cl$, 107-04-0; $Br(CH_2)_3Cl$, 109-70-6; $Br(CH_2)_2CHBrMe$, 107-80-2; $Br(CH_2)_4Cl$, 6940-78-9; $Br(CH_2)_5Br$, 111-24-0.