Table I. Reaction of Silver Salts with Alcohols

expt no.	substrate	amt, mmol	salt	amt, mmol	solvent(s)	vol, mL	source[a]	time	cell	% of theor silver ppted[b]
1	1,4-butanediol	5.56	$AgNO_3$	7.50	H_2O	30	laser	30 min	quartz	<10
2	1,4-butanediol	5.56	$AgNO_3$	7.50	H_2O	30	laser	30 min	Pyrex	<10
3	1,4-butanediol	5.56	$AgNO_3$	7.50	H_2O	30	Rayonet-1	24 h	quartz	<10
4	cyclohexanol	4.99	$AgNO_3$	7.50	H_2O	5	Rayonet-1	48 h	Pyrex	18
					Me_2SO	15				
5	cyclohexanol	4.99	$AgNO_3$	7.50	H_2O	5	Rayonet-1	48 h	quartz	11
					Me_2SO	15				
6	cyclohexanol	4.99	$AgNO_3$	7.50	H_2O	5	none	48 h	Pyrex	0
					Me_2SO	15				
7	cyclohexanol	99.8	$AgClO_4$	7.50	none		Rayonet-1	48 h	Pyrex	10
8	2-propanol	8.33	$AgNO_3$	7.50	H_2O	5	Rayonet-1	6 h	Pyrex	3
					Me_2SO	15				
9	2-propanol	416	AgOTs	*c*	none		Rayonet-1	24 h	Pyrex	5
10	ethanol	326	$AgNO_3$	7.50	Me_2SO	15	Rayonet-1	48 h	Pyrex	5
11	benzaldehyde	4.72	$AgNO_3$	7.50	H_2O	5	Rayonet-1	48 h	Pyrex	13
					Me_2SO	15				
12	none		$AgNO_3$	7.50	H_2O	5	Rayonet-1	24 h	Pyrex	12
					Me_2SO	15				
13	1,5-pentanediol	5.6	$AgNO_3$	16.8	H_2O	10	Rayonet-1	48 h	Pyrex	<5
14	1,5-pentanediol	5.6	$AgNO_3$	16.8	H_2O	10	Rayonet-1	8 h	quartz	<5
15	1,5-pentanediol	5.6	$AgNO_3$	16.8	H_2O	10	Rayonet-2	5 h	quartz	<5
16	1,5-pentanediol	5.6	$AgNO_3$	16.8	H_2O	10	Rayonet-2	6 h	Pyrex	<5
17	1-pentanol	100	$AgNO_3$	150	H_2O	75	sun lamp	48 h	Pyrex	<5
					Me_2SO	150				
18	1,5-pentanediol	5.6	$AgNO_3$	16.8	H_2O	10	none	3 days	Pyrex	slight silver mirror

[a] Laser: CR-18, UV line at 366.8 nm. Rayonet-1: low-pressure Hg, 350 nm. Rayonet-2: high-pressure Hg. All runs were preceeded by thorough degassing. [b] No precipitate with 2,4-DNPH was observed in any experiment except no. 11, nor was C=O absorption detected by IR; see text.[6] Yields of silver metal were determined gravimetrically. [c] Saturated solution.

Because the oxidation of an alcohol to a ketone (or aldehyde) is a two-electron process and Ag(I) is a one-electron oxidant, it was improbable that 7.5 mmol of silver ion could oxidize 5 mmol of an alcohol in 90% yield. Even more unlikely was the oxidation in 91% yield of 5.6 mmol of a *diol* (a four-electron process) by 8 mmol Ag(I). Our groups at Cincinnati and North Dakota State have attempted to reproduce these findings under a variety of conditions, and we have been unable to duplicate them. We are forced to conclude that some other adventitious oxidant must have been responsible for the reported observations.

Our experiments are summarized in Table I. As is readily apparent, there is no evidence for the photochemical oxidation of alcohols by Ag(I) for a number of substrate alcohols under a variety of irradiation conditions. Minor amounts of silver metal *do* appear after prolonged irradiation, but this is true even in the absence of alcohol substrate (experiment 12). The precipitation of silver is extremely slow in the absence of irradiation (experiments 6 and 18) and occurs more readily in aqueous Me_2SO than in pure Me_2SO or pure water (experiment 10).[5] In no case was ketone or aldehyde product detected by 2,4-DNPH[6] or IR, although test solutions containing the anticipated products easily revealed their presence. By contrast, we *were* able to reproduce the photochemical oxidation of alcohols with ferric ion.[7] Similar reactions with vanadium(III) have also been reported.[8]

Registry No. 1,4-Butanediol, 110-63-4; cyclohexanol, 108-93-0; 2-propanol, 67-63-0; ethanol, 64-17-5; benzaldehyde, 100-52-7; 1,5-pentanediol, 111-29-5; 1-pentanol, 71-41-0.

(5) The UV spectrum of silver nitrate in water or aqueous Me_2SO shows only weak end absorption in the 350-nm region (ϵ_{max} less than 0.2).
(6) Silver ion gives a precipitate with 2,4-DNPH (mp >300 °C). Tests for carbonyl were performed after first precipitating unreacted Ag(I) as silver chloride.
(7) V. I. Stenberg, S. P. Singh, N. K. Narain, and S. S. Palmer, *J. Org. Chem.*, **42**, 171 (1977).
(8) Y. Dor and M. Tsutsui, *J. Am. Chem. Soc.*, **100**, 3243 (1978).

Synthesis of (1*R*,9*S*)-13-Methyl-13-azatricyclo[7.3.1.0^{2,7}]trideca-2,4,6-triene. Observation of a Novel Deaminative Fragmentation

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A continuing effort has been devoted to the total synthesis of benzomorphans and nitrogen positional isomers of benzomorphan,[1] substances with morphine-like analgesic activity.[2] The recent development of opioid receptor binding procedures[3] has aroused renewed interest in the enantiomeric stereoselectivity of opioid receptors. We wish to report an asymmetric synthesis of a nitrogen positional isomer of benzomorphan and a novel fragmentation via cleavage of two α bonds to nitrogen atom which is encountered in the course of the synthesis.

The optically pure ester **1** ($[\alpha]^{24}_D$ −41.3° (*c* 1.0, EtOH)) is readily available from achiral homophthalic acid by asymmetric synthesis, which we have recently described.[4] Treatment of **1** with phosphorus pentasulfide afforded the thione **2** in 90% yield. Reaction of **2** with methyl bromoacetate afforded a crude imino thioether, to which structure **3** was assigned. Eschenmoser sulfur extrusion reaction[5] of the crude imino thioether **3** afforded the α,β-

(1) Recent reviews: (a) D. C. Palmer and M. J. Strauss, *Chem. Rev.*, **77**, 1 (1977); (b) D. Lednicer and L. A. Mitscher, "The Organic Chemistry of Drug Synthesis", Wiley-Interscience, New York, 1977, pp 286-312.
(2) For reviews, see P. S. Portoghese, *Acc. Chem. Res.*, **11**, 21 (1978).
(3) E. J. Simon, J. M. Hiller, and I. Edelman, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 1947 (1973); C. B. Pert and S. H. Snyder, *Science*, **179**, 1011 (1973).
(4) T. Wakabayashi and K. Watanabe, *Tetrahedron Lett.*, 4595 (1977); T. Wakabayashi and K. Watanabe, *ibid.*, 361 (1978).
(5) M. Roth, P. Dubs, E. Götschi, and A. Eschenmoser, *Helv. Chim. Acta*, **54**, 710 (1971).

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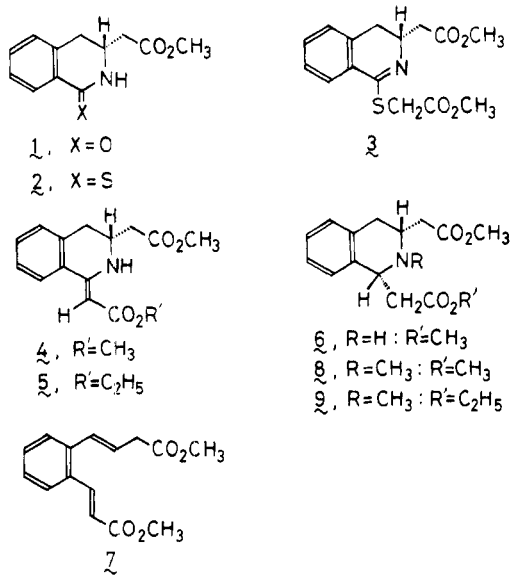
Chart I

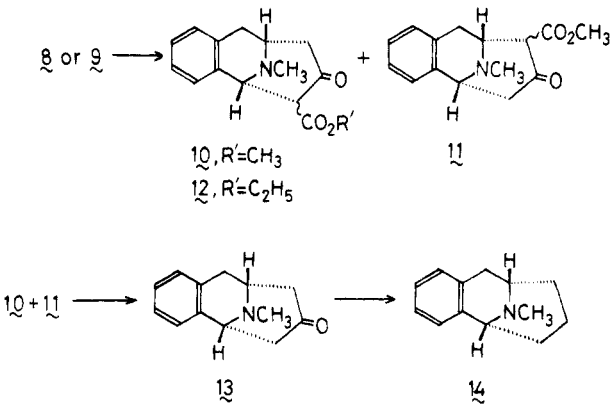


unsaturated ester **4** in 76% overall yield from **2** (Chart I). The *Z* configuration of the double bond in **4** was supported by the chemical shift (δ 5.21)[6] of its olefinic proton and also by the observation that the N–H absorption band of **4** in infrared spectrum did not shift upon its dilution in CCl_4, indicating a strong intramolecular hydrogen bonding between NH and C-1 ester oxygen.[8] Catalytic reduction of **4** gave the compound **6**, which is one diastereomer. In this reduction hydrogen attacked stereospecifically from the less hindered β side, as becomes evident later.

The reaction of **6** under Eschweiler–Clarke methylation conditions (37% HCHO, HCO_2H, reflux) led to a novel deaminative fragmentation to furnish, in one step, methyl (*E*)-4-[*o*-(2(*E*)-(methoxycarbonyl)vinyl)phenyl]-3-butenoate (**7**) in 73% overall yield from **4**. Presently we have not isolated the other fragment containing nitrogen. The central feature of this fragmentation is loss of the chirality in **6** and simultaneous gain of entropy in the extensively conjugated product **7**. Treatment of **6** with formic acid alone resulted in recovery of **6**. This fact indicates that formalin played an important role in the above fragmentation.[9]

Borch methylation[10] of **6** afforded the homogeneous N-methylated compound **8** in 52% overall yield from **4**. The N-methylated compound **8** did not afford the fragmentation product **7** with formic acid alone under reflux.

Scheme I



Dieckmann reaction of **8** yielded a mixture of cyclization products (**10** and **11**), hydrolytic decarboxylation of which with 6 N HCl gave the ketone **13** in 51% overall yield from **8**. The ring closure shown in Scheme I indicates that the side chains at C-1 and C-3 are in cis relationship, as mentioned before. In order to study the regioselectivity in the above Dieckmann cyclization, the compound **9**, in which the methyl ester group in the C-1 side chain of **8** is replaced by the ethyl ester group, was obtained by treatment of **2** with ethyl bromoacetate followed by the same sequence of reactions: (1) sulfur extrusion; (2) hydrogenation. The ethyl ester **9** was subjected to the same Dieckmann reaction conditions as **8** to yield a mixture of **11** and **12** (ratio of 12:11, ~2:1 by NMR spectroscopy).

Huang–Minlon reduction of **13** furnished (1*R*,9*S*)-13-methyl-13-azatricyclo[7.3.1.$0^{2,7}$]trideca-2,4,6-triene (**14**).

Experimental Section

Melting points were determined on a Yazawa micro melting point apparatus and were corrected. NMR spectra were recorded on a Varian EM-360 (60 MHz) or JEOL MH-100 (100 MHz) instrument with Me_4Si as an internal standard. IR spectra were recorded on a Hitachi EPI-S2 instrument. Mass spectra were obtained with a Shimazu LKB-9000 instrument. UV spectra were recorded on a Hitachi EPS-3P spectrometer. Optical rotations were measured with a JASCO DIP-SL automatic polarimeter. TLC was performed on precoated plates (Merck, alumina 150F–254, silica gel 60F–254).

(*R*)-3-[(Methoxycarbonyl)methyl]-1,2,3,4-tetrahydroisoquinoline-1-thione (2). (*R*)-3-[(Methoxycarbonyl)methyl]-3,4-dihydroisocarbostyril (**1**) (1.69 g), phosphorus pentasulfide (0.86 g), and benzene (350 mL) were refluxed for 2 h under N_2. After evaporation of the solvent, ice water was added to the residue. The mixture was extracted with CH_2Cl_2, and the solvent was removed in vacuo to give a residue which was chromatographed on silica gel. Fractions eluted with benzene–AcOEt (19:1) yielded 1.63 g (90%) of the thione **2**: mp 101–103 °C (EtOH); NMR (100 MHz, $CDCl_3$) δ 2.57–2.73 (m, 1 H), 2.83 (dd, 1 H, J = 8, 15 Hz), 3.15 (dd, 1 H, J = 5.5, 15 Hz), 3.69 (s, 3 H), 3.9–4.3 (m, 1 H), 7.06–7.45 (m, 3 H), 8.49 (dd, 1 H, J = 1.5, 7.5 Hz), 8.99 (br s, 1 H); IR ($CHCl_3$) 3395, 1736, 1583, 1500, 1439 cm^{-1}; $[\alpha]^{25}_D$ –26.6° (*c* 0.7, EtOH).

Anal. Calcd for $C_{12}H_{13}NO_2S$: C, 61.26; H, 5.53; N, 5.95. Found: C, 61.46; H, 5.55; N, 5.91.

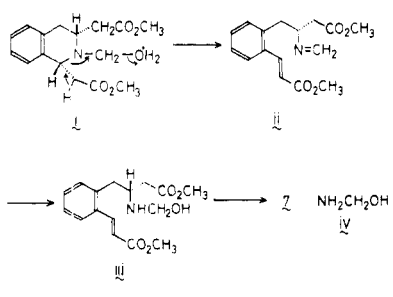
(*R*)-3-[(Methoxycarbonyl)methyl]-1-[(methoxycarbonyl)methylidene]-1,2,3,4-tetrahydroisoquinoline (4). To a solution of **2** (2.35 g) in dry CH_2Cl_2 (30 mL) was added a solution of methyl bromoacetate (1.3 mL) in dry CH_2Cl_2 (8 mL) at room temperature. After stirring for 3 h, the solvent was evaporated to give a residue which was dissolved in CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford 3.24 g of imino ester **3**: NMR (60 MHz, $CDCl_3$) δ 3.72 (s, 6 H), 3.81 (s, 2 H); IR ($CHCl_3$) 1739 cm^{-1}, the disappearance of the thione absorption band (1500 cm^{-1}). The crude imino ester **3** (3.24 g) was dissolved in a mixture of dry xylene (35 mL) and dry *t*-BuOH

(6) The calculated value according to the empirical equation[7] is δ 5.18 for *Z* olefin and δ 4.83 for *E* olefin.

(7) C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966).

(8) The molecular model examination reveals that a strong intramolecular hydrogen bonding can be formed only between NH and C-1 ester oxygen which are located in the same plane.

(9) Although a double fragmentation can be presented on the mechanism of this deaminative fragmentation, proof must wait for future work.



(10) R. E. Borch and A. I. Hassid, *J. Org. Chem.*, **37**, 1673 (1972).

(4.5 mL). To the solution was added Ph_3P (4.5 g) and *t*-BuOK (210 mg). The mixture was refluxed for 16 h. The reaction mixture was poured into ice water and extracted with CH_2Cl_2. The organic layer was washed with water and dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo to give a residue which was chromatographed on silica gel. Fractions eluted with benzene–AcOEt (19:1) gave 2.10 g (76% from **2**) of **4**: NMR (100 MHz, $CDCl_3$) δ 2.57 (d, 2 H, J = 7.5 Hz), 2.74 (dd, 1 H, J = 8.16 Hz), 3.04 (dd, 1 H, J = 5, 16 Hz), 3.68 (s, 3 H), 3.72 (s, 3 H), 3.8–4.1 (m, 1 H), 5.21 (s, 1 H), 7.1–7.75 (m, 4 H); IR (CCl_4) 3290, 1741, 1654, 1612, 1601, 1570 cm^{-1}; mass spectrum, m/e 275 (M^+), 202, 170 (base peak); UV (EtOH) λ_{max} (ϵ) 251 (14000), 333 nm (13000); $[\alpha]^{21}_D$ +46.6° (*c* 0.8, EtOH).

Methyl (*E*)-4-[*o*-(2(*E*)-(methoxycarbonyl)vinyl)-phenyl]-3-butenoate (7). A mixture of **4** (131 mg), PtO_2 (20 mg), and EtOH (10 mL) was hydrogenated under atmospheric pressure at room temperature for 1 h and filtered to remove the catalyst. The filtrate was evaporated to give 134 mg of (1*S*,3*R*)-1,3-bis-[(methoxycarbonyl)methyl]-1,2,3,4-tetrahydroisoquinoline (**6**). TLC showed principally one component (alumina, R_f 0.30, benzene–AcOEt (9:1); NMR (60 MHz, $CDCl_3$) δ 3.73 (s, 6 H); the NMR spectrum also indicated the absence of the other diastereomer; IR ($CHCl_3$) 1730 cm^{-1}. A solution of the crude **6** in 99% HCO_2H (0.3 mL) and 37% formalin (0.12 mL) was refluxed for 1 h. An excess of saturated $NaHCO_3$ was added to the reaction mixture, and the aqueous solution was extracted with ether. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated to give a residue which was chromatographed on silica gel. Fractions eluted with benzene–AcOEt (19:1) gave 90 mg of **7**, which showed a single spot on TLC (silica gel, R_f 0.37, benzene–AcOEt 9:1); NMR[11] (100 MHz, $CDCl_3$) δ 3.30 (d, 2 H, J = 7.5 Hz), 3.72 (s, 3 H), 3.80 (s, 3 H), 6.18 (dt, 1 H, J = 16, 7.5 Hz), 6.34 (d, 1 H, J = 16 Hz), 6.83 (d, 1 H, J = 16 Hz), 7.1–7.9 (m, 4 H), 8.03 (d, 1 H, J = 16 Hz); IR ($CHCl_3$) 1730 (shoulder), 1712 cm^{-1}; mass spectrum, m/e 260 (M^+), 228, 200, 141 (base peak); UV (EtOH) λ_{max} (ϵ) 246 (18900), 284 nm (17900); $[\alpha]^{24}_D$ 0° (*c* 0.3, EtOH). Analysis was carried out by high-resolution mass spectrometry; $C_{15}H_{16}O_4$ m/e (calcd) 260.1050, m/e (found) 260.1079.

(1*S*,3*R*)-1,3-Bis[(methoxycarbonyl)methyl]-2-methyl-1,2,3,4-tetrahydroisoquinoline (8). A mixture of **4** (2.05 g) and PtO_2 (0.2 g) in EtOH (200 mL) was reduced as above to give **6** (2.10 g). To a solution of **6** in a mixture of acetonitrile (24 mL) and 37% formalin (3.1 mL) was added $NaBH_3CN$ (764 mg) in three portions over 1 min. The mixture was stirred for 30 min, then acidified with AcOH to ca. pH 6, and further stirred for 30 min. After evaporation of the solvent, 2 N KOH (30 mL) was added to the residue and extracted with ether. A residue obtained on removal of the solvent was chromatographed on alumina. Fractions eluted with benzene–hexane (1:1) gave 1.13 g (52% from **4**) of **8**; TLC showed a single spot (alumina, R_f 0.46, benzene–AcOEt 9:1); NMR (100 MHz, $CDCl_3$) δ 2.26–3.2 (m, 7 H), 2.35 (s, 3 H), 3.67 (s, 6 H), 4.20 (t, 1 H, J = 7.5 Hz), 6.96–7.24 (m, 4 H); IR ($CHCl_3$) 1730 cm^{-1}; mass spectrum, m/e 291 (M^+), 176, 218 (base peak); $[\alpha]^{23}_D$ +14.8° (*c* 1.0, EtOH); high-resolution mass spectrometry for $C_{16}H_{21}NO_4$ m/e (calcd) 291.1471, m/e (found) 291.1484.

(1*R*,9*S*)-13-Methyl-13-azatricyclo[7.3.1.0^{2,7}]trideca-2,4,6-trien-11-one (13). A mixture of 215 mg of NaH (50% in mineral oil), **8** (635 mg), and toluene (8 mL) was refluxed for 3 h. To the reaction mixture was added a mixture of acetic acid (0.4 mL) and benzene (4 mL) under cooling in an ice bath, and, after stirring for 15 min, was added saturated aqeuous $NaHCO_3$ (15 mL). The mixture was extracted with CH_2Cl_2. The extract was dried, and the solvent was removed to give 647 mg of the cyclization products (**10** and **11**): NMR (60 MHz, $CDCl_3$) δ 3.80 (s), 3.83 (s). The above mixture (**10** and **11**) was refluxed in 6 N HCl (12 mL) for 2 h. The aqueous reaction mixture was washed with CH_2Cl_2–ether (1:2), then made alkaline by saturated $NaHCO_3$, and extracted with CH_2Cl_2–ether (2:1). A residue obtained on removal of the solvents was chromatographed on alumina. Fractions eluted with benzene–AcOEt (9:1) gave 229 mg (51%) of **13**: NMR (100 MHz, $CDCl_3$) δ 2.08–3.75 (m, 7 H), 2.58 (s, 3 H), 4.02–4.17 (m, 1 H), 6.8–7.3 (m, 4 H); IR ($CHCl_3$) 1713 cm^{-1}; mass spectrum, m/e 201 (M^+), 144 (base peak); $[\alpha]^{20}_D$ +41.9° (*c* 0.69, EtOH).

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.46; H, 7.47; N, 6.76.

Preparation of (1*S*,3*R*)-1-[(Ethoxycarbonyl)methyl]-2-methyl-3-[(methoxycarbonyl)methyl]-1,2,3,4-tetrahydroisoquinoline (9) and Dieckmann Cyclization of 9. The compound **9** was prepared in 40% yield from **2** by the same procedure as for the preparation of **8** from **2**. The thione **2** (940 mg) was treated with ethyl bromoacetate, followed by sulfur extrusion reaction, to yield 784 mg (68%) of (*R*)-1-[(ethoxycarbonyl)-methylidene]-3-[(methoxycarbonyl)methyl]-1,2,3,4-tetrahydroisoquinoline (**5**): NMR (60 MHz, $CDCl_3$) δ 1.27 (t, 3 H, J = 7 Hz), 3.72 (s, 3 H), 4.20 (q, 1 H, J = 7 Hz), 5.25 (s, 1 H); IR ($CHCl_3$) 3290, 1735, 1642, 1570 cm^{-1}. The α,β-unsaturated ethyl ester **5** (450 mg) underwent catalytic hydrogenation, followed by Borch methylation, to give 279 mg (59%) of **9**: NMR (60 MHz, $CDCl_3$) δ 1.23 (t, 3 H, J = 7 Hz), 2.35 (s, 3 H), 3.69 (s, 3 H), 4.18 (q, 2 H, J = 7 Hz); IR ($CDCl_3$) 1728 cm^{-1}; $[\alpha]^{21}_D$ +15.0° (*c* 1.0, EtOH). A mixture of **9** (240 mg), NaH (76 mg, 50% in mineral oil), and toluene (3 mL) was refluxed for 7 h and was worked up as described in the preparation of **13** to afford a mixture of the cyclized compounds, **11** and **12** (210 mg): NMR (60 MHz, $CDCl_3$) δ 3.80 (s, OCH_3), 3.83 (s, OCH_3), 4.30 (q, OCH_2CH_3). The ratio of **12** to **11**, ~2:1, was calculated from the integrated NMR peak areas of the methyl signals of **12** and the ethylene signal of **11**.

(1*R*,9*S*)-13-Methyl-13-azatricyclo[7.3.1.0^{2,7}]trideca-2,4,6-triene (14). To a mixture of **13** (136 mg) and triethylene glycol (6 mL) was added 80% hydrazine hydrate (0.87 mL) and KOH (0.87 g). The mixture was heated at 130 °C on an oil bath and then at 210 °C by gradually raising the bath temperature to 210 °C over 1 h. The mixture was heated at this temperature for 2 h and cooled, and water was added. The mixture was extracted with CH_2Cl_2. The extract was dried and the solvent was removed to give a residue which was chromatographed on alumina. Fractions eluted with benzene gave 104 mg (82%) of **14**: NMR (100 MHz, $CDCl_3$) δ 1.0–2.6 (m, 7 H), 2.23 (s, 3 H), 3.0–3.4 (m, 2 H), 3.68–3.82 (m, 1 H), 6.86–7.3 (m, 4 H); IR ($CHCl_3$) 2930, 1482, 1445, 1366, 1127, 1088 cm^{-1}; mass spectrum, m/e 187 (M^+), 144 (base peak); $[\alpha]^{20}_D$ +76.4° (*c* 0.52, EtOH); hydrobromide salt mp 247–248 °C (MeOH–acetone). Anal. Calcd for $C_{13}H_{18}BrN$: C, 58.22; H, 6.77; N, 5.22. Found: C, 57.92; H, 6.79; N, 5.11. Picrate: mp 202–204 °C (MeOH–ether). Anal. Calcd for $C_{19}H_{20}N_4O_7$: C, 54.80; H, 4.84; N, 13.46. Found: C, 55.13; H, 4.70; N, 13.18.

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Registry No. **1**, 66520-42-1; **2**, 69303-81-7; **3**, 72161-36-5; **4**, 72161-37-6; **5**, 72161-38-7; **6**, 72161-39-8; **7**, 72161-40-1; **8**, 72161-41-2; **9**, 72161-42-3; **10**, 72161-43-4; **11**, 72161-44-5; **12**, 72161-45-6; **13**, 72161-46-7; **14**, 72161-47-8; **14**·HBr, 72203-30-6; methyl bromoacetate, 96-32-2; ethyl bromoacetate, 105-36-2.

(11) The ^1H NMR decoupling experiment of **7** revealed that the pair of protons assignable to δ 6.18, 6.83 and the other pair of protons assignable to δ 6.34, 8.03 coupled each other.