H/H + D ratio in every species of the exchanging system can be given by eq 5.

$$\frac{3[CH_3]_{stoich}}{5/3[DFSO_3]_{stoich}} = \frac{[DFSO_3]_{stoich}}{5/3[DFSO_3]_{stoich}} = 3/5 \qquad (5)$$

Accordingly, the final average number of hydrogens in C_3H_7 should be $4 + 3^3/_5 = 5.8$ and the final C_3H_7/NH_2 ratio: $5.8/2 = 2.9$. However, the experimentally observed C_3H_7/NH_2 integral ratio falls below this limit (2.3), suggesting that additional processes must be operative which remove C_3H_7.

We are currently exploring these exchange phenomena in more detail by ^2D and ^{13}C NMR.

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Registry No. 1, 102283-88-5; 2, 102283-89-6; 3, 102283-90-9; 4, 102283-91-0; *n*-propylamine, 107-10-8; *n*-butylamine, 109-73-9; *n*-pentylamine, 110-58-7; *n*-octylamine, 111-86-4; hydrogen, 1333-74-0.

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[2 + 2] Cycloaddition of Sulfonyl and Acyl Isocyanates to Glycals

Summary: [2 + 2] Cycloaddition of sulfonyl and acyl isocyanates **1–3** to glycals **4–8** proceeds stereospecifically to afford the β-lactam ring anti with respect to the C-3 substituent. Unblocking of the electron-withdrawing N-substituent produces the relatively stable β-lactams.

Sir: [2 + 2] cycloaddition of active isocyanates to 3,4-dihydro-2*H*-pyran derivatives has already been attempted several times,[1-5] but in only a few cases were the corresponding β-lactams obtained.[1,2,5] Simple derivatives of 3,4-dihydro-2*H*-pyran afforded open-chain α,β-unsaturated amides,[1-5] whereas tri-*O*-acetyl-D-glucal was found to be unreactive.[6] It can be assumed that the nature of substituents attached to the dihydropyran ring determines the equilibrium state of this reversible cycloaddition,[7-9] which in the case of acetylated glycals under normal pressure is entirely shifted toward substrates.[6] Application of 10 kbar pressure, however, resulted in cycloaddition of tosyl and trichloroacetyl isocyanate (**1** and **3**) to acetylated glycals and led to the formation of unstable β-lactams.[7-9]

Assuming that thermodynamics controls product formation in these reactions, we chose to investigate the cycloaddition of isocyanates **1–3** to glycals **4–8** having nonpolar blocking groups, under normal pressure. The reactions were performed in absolute $CDCl_3$ at room temperature and were monitored by ^1H NMR spectroscopy.[10]

Cycloaddition of **1** and **2** (3 molar equiv) to glycals **4–8** (1 equiv) proceeds regio- and stereospecifically with formation of the β-lactam ring anti to the C-3 substituent (Scheme I). Tosyl isocyanate (**1**) gives the respective β-lactams **9** after 6–40 h in 75–90% yield (Table I). The isocyanate **2** is more reactive under the same conditions. Cycloaddition to all glycals **4–8** is completed in about 2 h, affording **9**; thereafter slow decomposition of product is observed. After 20 h substantial amounts (10–60%) of the respective α,β-unsaturated amide **10** is detected.

Trichloroacetyl isocyanate (**3**) reacts with **4–8** more slowly than sulfonyl isocyanates **1** and **2**. Reactions are completed in about 50 h to produce [2 + 2] cycloadducts **9**, [4 + 2] **11**, and the open-chain amide **10**. In agreement with our earlier findings, **3** adds anti to the C-3 substituent to give cis-fused bicyclic systems **9** and **11**. The proportion of products **9**:**10**:**11** depends on the reaction time and glycal used. For example, **5** affords after 6 h about 12% of **9a** and 18% of **11a**, whereas after 50 h **9a** becomes the main component (50%) of the mixture and is accompanied by 32% of **10a** and 18% of **11a**. On the other hand, glycals **7** and **8** furnish [4 + 2] cycloadducts **11b** which are more stable than the β-lactams **9b** (Table I).

Our experiments clearly point to low stability of cycloadducts **9**. This is certainly caused by an electron-withdrawing group attached to the nitrogen atom. Therefore N-deprotection is necessary before isolation or chemical transformation of **9** are undertaken. Until now attempts to split the sulfonyl substituent without decomposition of the β-lactam ring in **9** were unsuccessful. In case of the trichloroacetyl protecting group, analogously to the trifluoroacetyl group,[4] addition of benzylamine to the reaction mixture leads to removal of the N-protection to afford stable bicyclic β-lactams. Compounds **12**, **13**, and **14** were isolated from respective post-reaction mixtures by silica gel chromatography in 30%, 50%, and 40% yield, respectively. Further deprotection with the hydrogen fluoride–pyridine 1:1 complex in THF affords crystalline, stable, water-soluble β-lactams **15** and **16**.[11]

(1) Effenberger, E.; Gleiter, R. *Chem. Ber.* **1964**, *97*, 1576.
(2) Barrett, A. G. M.; Fenwick, A.; Betts, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 299.
(3) Chan, J. H.; Hall, S. S. *J. Org. Chem.* **1984**, *49*, 195.
(4) Barrett, A. G. M.; Betts, M. J.; Fenwick, A. *J. Org. Chem.* **1985**, *50*, 169.
(5) Chitwood, J. L.; Gott, P. G.; Martin, J. C. *J. Org. Chem.* **1971**, *36*, 2228.
(6) Hall, R. H.; Jordan, A.; Laurens, G. J. *J. Chem. Soc. Perkin Trans. 1* **1973**, 38. Hall, R. H.; Jordan, A.; de Villiers, O. G. *Ibid.* **1975**, 626.
(7) Chmielewski, M.; Kałuza, Z.; Bełzecki, C.; Sałanski, P.; Jurczak, J. *Tetrahedron Lett.* **1984**, *25*, 4797.
(8) Chmielewski, M.; Kałuza, Z.; Bełzecki, C.; Sałanski, P.; Jurczak, J.; Adamowicz, H. *Tetrahedron* **1985**, *41*, 2441.
(9) Chmielewski, M.; Kałuza, Z.; Bełzecki, C.; Sałanski, P.; Jurczak, J., in press.

(10) The compounds **9** and **11** were characterized by chemical shifts and coupling constants for protons H-1 and H-2, whereas the amides **10** were characterized by chemical shifts of H-1 proton. For example, adducts derived from **3** and **4**: **9a** [6.02 (d, 1 H, J_{12} = 5.5 Hz, H-1), 3.47 (dd, 1 H, J_{23} = 3.0 Hz, H-2)] and **11a** [6.15 (d, 1 H, J_{12} = 3.7 Hz, H-1), 2.94 (dd, 1 H, J_{23} = 9.0 Hz, H-2)]; adducts derived from **2** and **4**: **9a** [5.95 (d, 1 H, J_{12} = 5.6 Hz, H-1), 3.40 (dd, 1 H, J_{23} = 3.2 Hz, H-2)] and **10a** [7.60 (s, 1 H, H-1)]. The composition of the reaction mixture was determined by the integration of the respective signals.

(11) **12**: mp 50–54 °C; $[\alpha]_D$ +61.5° (*c* 1, CH_2Cl_2); IR (film) 1760 cm^{-1}; ^1H NMR ($CDCl_3$) 5.30 (d, 1 H, J_{12} = 4.6 Hz, H-1), 3.08 (dt, 1 H, $|J_{12} + J_{23}|$ = 6.0 Hz, H-2). **13**: mp 74–76 °C; $[\alpha]_D$ −5.7° (*c* 1, CH_2Cl_2); IR ($CHCl_3$) 3410, 1775 cm^{-1}; ^1H NMR (CCl_4) 5.40 (d, 1 H, J_{12} = 4.6 Hz, H-1), 3.15 (m, 1 H, H-2). **14**: mp 53–57 °C; $[\alpha]_D$ −53.5° (*c* 1, CH_2Cl_2); IR ($CHCl_3$) 3410, 1775 cm^{-1}; ^1H NMR (CCl_4) 5.30 (d, 1 H, J_{12} = 4.3 Hz, H-1), 3.12 (m, 1 H, H-2). **15**: mp 179–180 °C; $[\alpha]_D$ +65.4° (*c* 1, H_2O); IR (Nujol) 3320, 1715 cm^{-1}; ^1H NMR (Me_2SO-d_6) 5.50 (d, 1 H, J_{12} = 4.0 Hz, H-1), 3.20 (m, 1 H, H-2). **16**: mp 170–171 °C; $[\alpha]_D$ −112.4° (*c* 1, H_2O); IR (Nujol) 3380, 3240, 1750 cm^{-1}; ^1H NMR (Me_2SO-d_6) 5.28 (d, 1 H, J_{12} = 4.2 Hz, H-1), 3.13 (t, 1 H, H-2).

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Scheme I

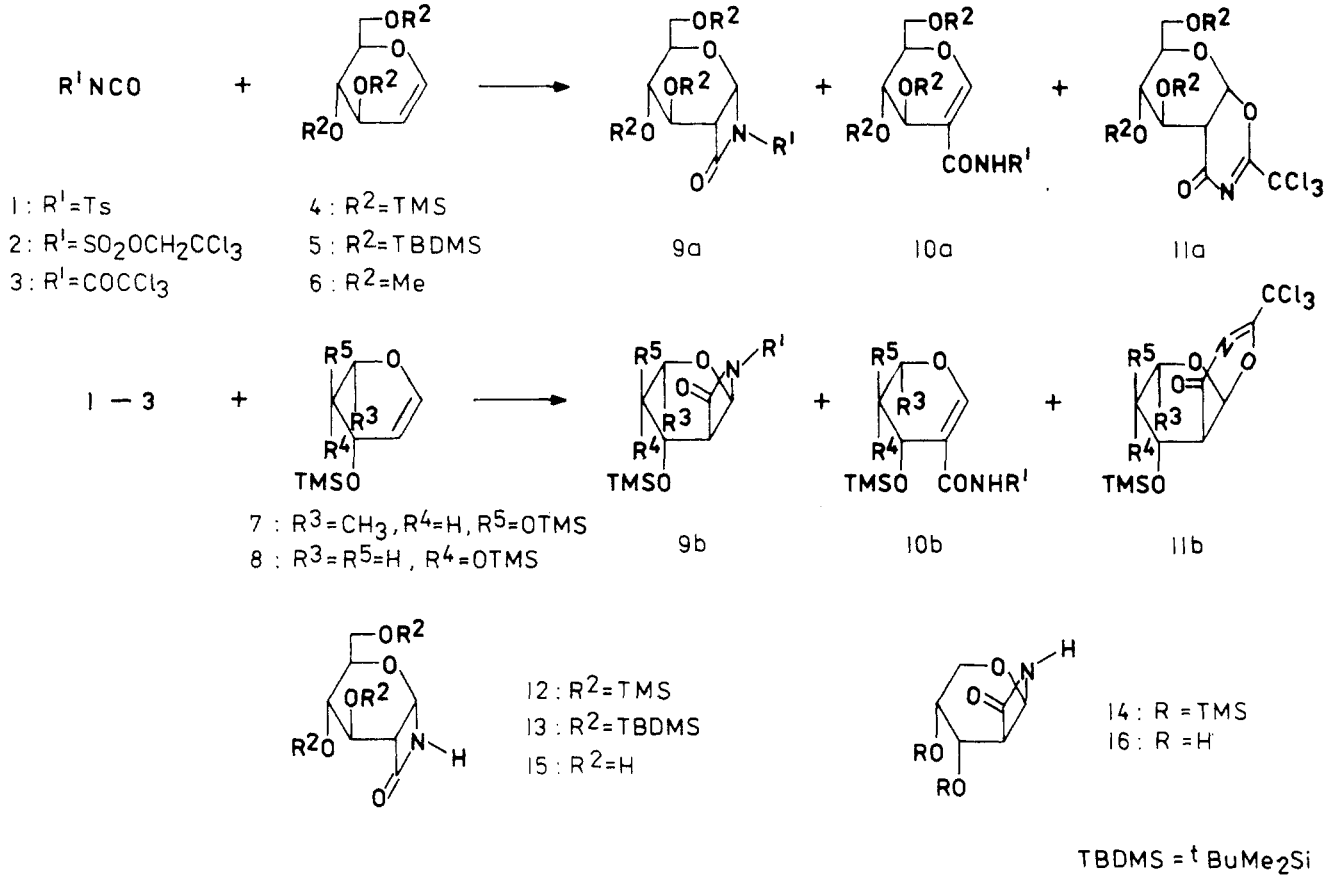

Table I

		compositn of the reactn mixture (%)											
		2 h			6 h			22 h			50 h		
glycal	isocyanate	**9**	**10**	**11**	**9**	**10**	**11**	**9**	**10**	**11**	**9**	**10**	**11**
4	1	55			77			76			75		
	2	100			90	10			decomp				
	3	10		15	25		40	35		65	35		65
5	1	14			37			50			90		
	2	100			100				decomp				
	3	2		3	12		18	28	25	26	50	32	18
6	1	17			41			75			71		
	2	100							decomp				
	3		9 + 11 = 10			9 + 11 = 25		19		47	19	7	74
7	1	59			73			75			72		
	2	100							decomp				
	3	8		18	23		51	23	7	70	10	5	85
8	1	69			75			78			74		
	2	100						10	50	decomp			
	3	27		31	42		50	20	4	76	7	5	88

Avoidance of application of high pressure technique makes the present synthesis very attractive and experimentally simple.

In conclusion we have demonstrated that introduction of nonpolar blocking groups to the glycal moiety shifts the equilibrium state of the [2 + 2] cycloaddition of active isocyanates toward bicyclic β-lactams. Isocyanates such as phenyl isocyanate or methyl isocyanatoacetate are unreactive with glycals **4**–**8** even under high pressure. Enhancement of the reactivity of isocyanates causes lower stability of the azetidinone ring and promotes rearrangement ot the α,β-unsaturated amide. This is well visible if one compares the reactivity of *N*-tosyl β-lactams vs. that of *N*-(trichloroethoxy)sulfonyl compounds.

The studies presented herein provide the basic information necessary for the further utilization of the [2 + 2] cycloaddition of isocyanates to glycals.

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Registry No. 1, 4083-64-1; 2, 22959-55-3; 3, 3019-71-4; 4, 63914-19-2; 5, 79999-47-6; 6, 16740-98-0; 7, 101997-92-6; 8, 102129-56-6; **9a** (R¹ = Ts, R² = TMS), 101979-61-7; **9a** (R¹ = $SO_2OCH_2CCl_3$, R² = TMS), 101979-62-8; **9a** (R¹ = $COCCl_3$, R² = TMS), 101979-63-9; **9a** (R¹ = Ts, R² = TBDMS), 100924-13-8; **9a** (R¹ = $SO_2OCH_2CCl_3$, R² = TBDMS), 101979-65-1; **9a** (R¹ = $COCCl_3$, R² = TBDMS), 101979-66-2; **9a** (R¹ = Ts, R² = Me), 101979-69-5; **9a** (R¹ = $SO_2OCH_2CCl_3$, R² = Me), 101979-70-8; **9a** (R¹ = $COCCl_3$, R² = Me), 101979-71-9; **9b** (R¹ = Ts, R³ = Me, R⁴ = H, R⁵ = OTMS), 101979-74-2; **9b** (R¹ = $SO_2OCH_2CCl_3$, R³ = Me, R⁴ = H, R⁵ = OTMS), 101979-75-3; **9b** (R¹ = $COCCl_3$, R³

= Me, R^4 = H, R^5 = OTMS), 101979-76-4; **9b** (R^1 = Ts, R^3 = R^5 = H, R^4 = OTMS), 101979-79-7; **9b** (R^1 = $SO_2OCH_2CCl_3$, R^3 = R^5 = H, R^4 = OTMS), 101979-80-0; **9b** (R^1 = $COCCl_3$, R^3 = R^5 = H, R^4 = OTMS), 101979-81-1; **10a** (R^1 = $SO_2OCH_2CCl_3$, R^2 = TMS), 101997-93-7; **10a** (R^1 = $COCCl_3$, R^2 = TBDMS), 101979-67-3; **10a** (R^1 = $COCCl_3$, R^2 = Me), 101979-72-0; **10b** (R^1 = $COCCl_3$, R^3 = Me, R^4 = H, R^5 = OTMS), 101979-77-5; **10b** (R^1 = $COCCl_3$, R^3 = R^5 = H, R^4 = OTMS), 101979-82-2; **11a** (R^2 = TMS), 101979-64-0; **11a** (R^2 = TBDMS), 101979-68-4; **11a** (R^2 = Me), 101979-73-1; **11b** (R^3 = Me, R^4 = H, R^5 = OTMS), 101979-78-6; **11b** (R^3 = R^5 = H, R^4 = OTMS), 101979-83-3; **12**, 101979-84-4; **13**, 101979-85-5; **14**, 101979-87-7; **15**, 101979-86-6; **16**, 101979-88-8.

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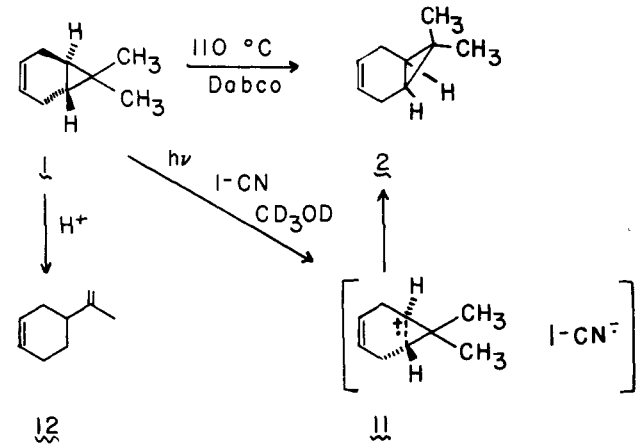
Synthesis and Photoinduced Electron-Transfer Promoted Isomerization of 7,7-Dimethyl-*trans*-bicyclo[4.1.0]hept-3-ene

Summary: The title compound, **1**, is highly reactive (very sensitive to acid, and, thermally isomerized to the cis isomer **2**, at 110 °C); photosensitized isomerization of **1** to **2** is effected by the excited state of 1-cyanonaphthalene.

Sir: Since it was first suggested that small, trans-fused bicyclic molecules should have unique bonding,[1] numerous attempts have been made to bridge the cyclopropyl moiety with a short carbon–carbon chain in a trans configuration.[2-5] Recently, we reported a simple approach to *trans*-bicyclo[4.1.0]hept-3-ene.[6] We now report the first synthesis of 7,7-dimethyl-*trans*-bicyclo[4.1.0]hept-3-ene (**1**). In addition, we have found that **1** was rapidly isomerized to 7,7-dimethyl-*cis*-bicyclo[4.1.0]hept-3-ene (**2**) in the presence of excited state 1-cyanonaphthalene (1-CN).

The synthesis of **1** involved a major modification of our earlier synthetic approach to the intriguing *trans*-bicyclo[4.1.0]heptyl skeleton. As shown in Scheme I, Fisher esterification of commercial *trans*-β-hydromuconic acid (**3**)[7] gave an 85% yield of dimethyl *trans*-hex-3-ene-1,6-dioate (**4**).[8] Subsequent reduction of **4** with lithium aluminum hydride produced the diol, **5**, in 82% yield.[9] Treatment of **5** with carbon tetrabromide and triphenylphosphine gave **6**[9] in 85% yield. Phase-transfer-catalyzed addition of dibromocarbene to **6** using bromoform, sodium hydroxide, and triethylbenzylammonium chloride (as phase-transfer agent)[10] yielded 85% of the tetrabromide **7**.[11] Utilizing high dilution techniques, **7** was allowed to react with sodium sulfide to give 68% of 8,8-dibromo-4-thia-*trans*-bicyclo[5.1.0]octane (**8**). When **8** was allowed to react with a tenfold excess of lithium dimethylcuprate,[12] a 97% yield of a 47:53 mixture of **9** and its monomethylated counterpart, 8-methyl-4-thia-*trans*-bicyclo[5.1.0]octane, was obtained. The two cyclic sulfides were separated by preparative MPLC to give a 36% yield of **9**. Conversion of the sulfide to an α-chlorosulfone was accomplished in a two-step process involving treatment of **9** with *N*-chlorosuccinimide to α-chlorinate and then with *m*-chloroperbenzoic acid to oxidize the sulfide linkage to a sulfone. The mixture of stereoisomers represented by **10** was obtained in 90% yield. When **10** was treated with 5 equiv of potassium *tert*-butoxide in dimethyl sulfoxide, **1** was produced in 45% yield[13] for an overall yield of 5.0%.

The structure of **1** was established on the basis of spectral data and by its facile conversion to 7,7-dimethyl-*cis*-bicyclo[4.1.0]hept-3-ene (**2**) both thermally and photochemically. The ^1H NMR of **1** in benzene-d_6 showed: δ 5.96 (s, 2 H), 2.55 (dd, 2 H), 2.00 (m, 2 H), 1.10 (s, 6 H), and −0.50 (m, 2 H); ^{13}C NMR (C_6D_6) δ 131.61 (d), 32.49 (s), 31.76 (t), 30.99 (d), and 23.25 (q). The upfield position of the two bridgehead protons at δ = −0.50 was consistent with the similar position found for these protons in the nonmethylated parent hydrocarbon.[6] Thermally, **1** was converted into **2** at 110 °C in 93% yield.[14] This thermal



(1) Gassman, P. G. *J. Chem. Soc., Chem. Commun.* **1967**, 793.
(2) Cope, A. C.; Hecht, J. K. *J. Am. Chem. Soc.* **1963**, *85*, 1780. Corey, E. J.; Schulman, J. I. *Tetrahedron Lett.* **1968**, 3655. DePuy, C. H.; Marshall, J. L. *J. Org. Chem.* **1968**, *33*, 3326. Moshuk, G.; Petrowski, G.; Winstein, S. *J. Am. Chem. Soc.* **1968**, *90*, 2179. Gassman, P. G.; Williams, E. A.; Williams, F. J. *Ibid.* **1971**, *93*, 5199. Wiberg, K. B.; Nakahira, T. *Ibid.* **1971**, *93*, 5193. Wiberg, K. B.; Nakahira, T. *Tetrahedron Lett.* **1970**, 3759. Deyrup, J. A.; Betkouski, M. F. *J. Org. Chem.* **1975**, *40*, 284. Wiberg, K. B.; de Meijere, A. *Tetrahedron Lett.* **1969**, 59. Deyrup, J. A.; Betkouski, M.; Szabo, W.; Mathew, M.; Palenik, G. J. *J. Am. Chem. Soc.* **1972**, *94*, 2147.
(3) (a) Gassman, P. G.; Williams, F. J.; Seter, J. *J. Am. Chem. Soc.* **1968**, *90*, 6893. (b) Kirmse, W.; Hase, Ch. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 891. (c) Wiberg, K. B.; de Meijere, A. *Tetrahedron Lett.* **1969**, 519. (d) Ashe, A. J., III. *Ibid.* **1969**, 523. (e) Gassman, P. G.; Seter, J.; Williams, F. J. *J. Am. Chem. Soc.* **1971**, *93*, 1673. (f) Gassman, P. G.; Williams, F. J. *Ibid.* **1971**, *93*, 2704. (g) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 332. (h) Pirkle, W. H.; Lunsford, W. B. *J. Am. Chem. Soc.* **1972**, *94*, 7201.
(4) Paukstelis, J. V.; Kao, J.-L. *J. Am. Chem. Soc.* **1972**, *94*, 4783. Paukstelis, J. V.; Kao, J.-L. *Tetrahedron Lett.* **1970**, 3691.
(5) A second derivative of *trans*-bicyclo[4.1.0]heptane has been reported as a nonisolable intermediate. See: Casadevall, E.; Pouet, Y. *Tetrahedron* **1978**, *34*, 1921. For an example of an unsuccessful attempt to prepare a *trans*-bicyclo[4.1.0]hept-3-ene derivative by an acyloin condensation, see: Delbaere, C. U. L.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1974**, 879. See also: Blancou, H.; Casadevall, E. *Tetrahedron* **1976**, *32*, 2907. For an additional unsuccessful approach see ref 3g.
(6) Gassman, P. G.; Bonser, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 667. See also: Gassman, P. G.; Bonser, S. M. *Tetrahedron Lett.* **1983**, *24*, 3431.
(7) Available from Aldrich Chemical Co., Inc.
(8) Linstead, R. P.; Owen, L. N.; Wells, R. J. *J. Chem. Soc.* **1953**, 1225.
(9) Lukes, R.; Dudek, V. *Collect. Czech. Chem. Commun.* **1959**, *24*, 2484.
(10) The phase-transfer conditions used are essentially those described in the literature. Makosza, M.; Fadorynski, M. *Synth. Commun.* **1973**, 305.
(11) Satisfactory elemental analyses and/or exact mass molecular weights have been obtained on all new compounds shown. Spectral data were consistent with the assigned structures in all cases. All yields are of purified materials.
(12) Corey, E. J.; Posner, G. *J. Am. Chem. Soc.* **1967**, *89*, 3911.
(13) This classical Ramberg–Bäcklund reaction was carried out at ambient temperature. For a review, see: Paquette, L. A. *Org. React. (N.Y.)* **1977**, *25*, 1.

0022-3263/86/1951-2397$01.50/0