and 5% KOH, and could be purified by reprecipitating from a DMF solution into acetone followed by a second reprecipitation from DMF into water. The purified polymer exhibited η_{inh} = 0.132 in DMF and decomposed upon heating to 220°. *Anal.* Calcd for $C_{14}H_{20}N_4O_6S$: C, 39.5; H, 4.70; N, 13.14. Found: C, 40.63; H, 5.01; N, 13.58.

Investigation of the $AlCl_3$-*n*-Butyl Isocyanate Complex. A 0.1 *M* stock solution of *n*-butyl isocyanate in nitrobenzene was used for all of the measurements. A 1.0 *M* solution of $AlCl_3$ in nitrobenzene was used to prepare a second 0.1 *M* stock solution and these two solutions were used to prepare complex solutions where the concentration of $AlCl_3$ ranged from 0.005 to 0.5 *M* and the concentration of *n*-butyl isocyanate was held constant at 0.05 *M*. The complex solutions were allowed to stand at 25° for at least 30 min before the infrared spectra were recorded with a Perkin-Elmer Model 621 spectrometer. The spectra of the solutions were measured at ambient temperature in matched 0.4-mm sodium chloride cells using nitrobenzene as a reference.

Registry No.—*n*-Butyl isocyanate, 111-36-4; hexamethylene diisocyanate, 822-06-0; poly(benzene-1,4-disulfonylhexamethyleneurea), 51002-85-8; benzene-1,4-disulfonamide polymer with hexamethylene diisocyanate, 51002-86-9.

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Communications

Synthesis *via* Oxazolines. V. A Simultaneous Kinetic Resolution of *sec*-Alkyl Iodides and Synthesis of Optically Active 3-Alkylalkanoic Acids. A Method for Determination of Absolute Configuration and Maximum Optical Rotations

Summary: Reaction of racemic *sec*-alkyl iodides with a chiral oxazoline carbanion results in 30–40% stereoselective alkylation of the S enantiomer of the halide and allows recovery of *R*-enriched halide.

Sir: We recently reported the use of chiral nonracemic oxazolines in the asymmetric synthesis of α-methylalkanoic acids.[1] Further studies on the 2-methyl derivative **1** of this heterocyclic system have now revealed that it is capable of chiral recognition in nucleophilic substitution of *sec*-alkyl halides resulting in simultaneous formation of optically active halides and 3-methylalkanoic acids *via* kinetic resolutions.[2]

Treatment of **1**[3] with 1.0 equiv of lithium diisopropylamide (LDA) gave the lithio salt **2** (THF, −78°). Addition of 2.0 equiv of racemic 2-iodoalkanes (−40 to −60°, 6–8 hr) produced, after quenching, the alkylated oxazoline **3** in 92–96% yield along with recovered iodoalkane **4** which was 25–30% optically pure and possessed the *R* configuration (Table I). Hydrolysis (3 *N* HCl, 2 hr) of the alkylated oxazoline **3** afforded the 3-methylalkanoic acids **5** in comparable (±3%) optical purity and also possessing the *R* configuration (Table I). Aside from the asymmetric synthesis of the carboxylic acids and the kinetic resolution of the halides in moderate optical yields, this technique offers a rather significant dividend. *It should be feasible to predict, within a few per cent, the maximum rotation of one of the reaction products (halide or acid) provided that the other is known.* This prediction is substantiated by the following events. Reaction of **1** with 2.0 equiv of racemic 2-iodooctane gave recovered halide (*R*)-**4** (R = hexyl) in 85% yield with an optical purity of 24–30% (Table I). However, the carboxylic acid (*R*)-**5** was formed in 53% optical purity based upon a reported value of −4.7°

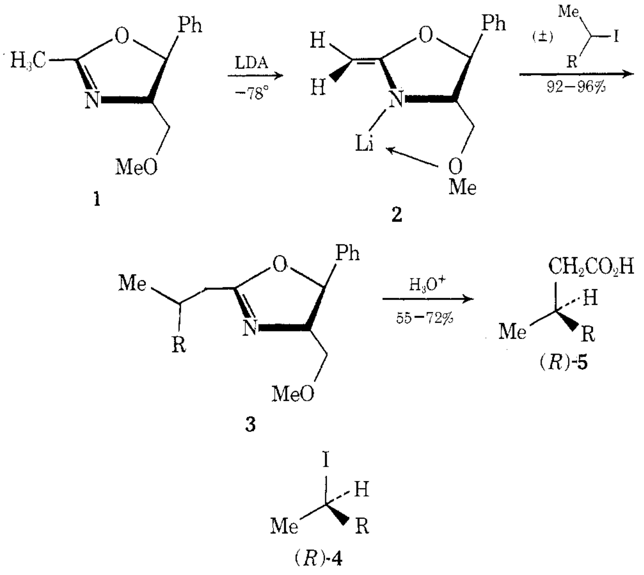


Table I
Optically Active *sec*-Alkyl Iodides, (*R*)-4, and 3-Methylalkanoic Acids, (*R*)-5

Iodide **4**,[a,b] R	$[\alpha]_D^{25}$ (neat), degree	Optical purity,[c] %	Acid **5**,[a] R	$[\alpha]_D^{25}$ (neat), degree	Optical purity, %
Et	−9.4	27–29[d]	Et	−2.6	31[e]
n-Propyl	−10.6	24–29	*n*-Propyl	+0.7	26–28[e]
n-Hexyl	−15.0	25–30[f]	*n*-Hexyl	+2.4	34[g]

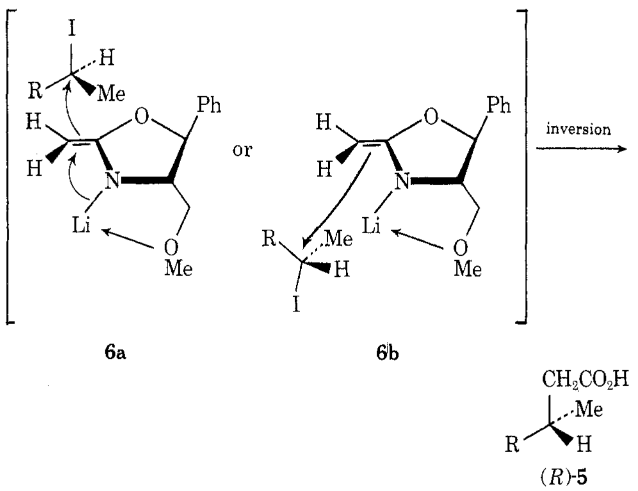
[a] Recovered in 81–96% yield. [b] To avoid enrichment by fractionating, all materials were distilled to <10% of residue. [c] Based upon highest values reported: **2-iodobutane,** $[\alpha]_D$ −31.98° (neat), and **2-iodopentane** $[\alpha]_D$ −37.15° (neat), R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99,** 45 (1911); $[\alpha]_D$ 46.7° (neat), D. H. Brauns, *Recl. Trav. Chim. Pays-Bas*, **65,** 799 (1946); **2-iodooctane,** $[\alpha]_D$ −59.5° and +62.6° (neat), M. C. Berlak and W. Gerrard, *J. Chem. Soc.*, 2309 (1949). [d] Contained 15–20% of THF formed as an azeotropic mixture. [e] Based on highest values reported: **3-methylpentanoic acid,** $[\alpha]_D$ −8.92° (neat), P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **92,** 456 (1931); **3-methylhexanoic acid,** $[\alpha]_D$ +2.50° (neat), I. A. Holiday and N. Polgar, *J. Chem. Soc.*, 2934 (1957), and $[\alpha]_D$ +2.77° (neat), P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **92,** 456 (1931). [f] Contained 6–8% octenes which accounted for the lower value as compared to the corresponding acid. [g] **3-Methylnonanoic acid** is reported to have $[\alpha]_D$ −4.71° (neat), A. Rothen and P. A. Levene, *J. Chem. Phys.*, **7,** 975 (1939). Optical purity is based on +7.1° obtained in this work.

(Table I, ref *g*). To preclude any error in the reported maximum rotation of either the iodide **4** or the acid **5**, the alkylation of **1** was repeated using (+)-2-iodooctane[4] (70% optical purity, 1.8 equiv). The recovered iodide had $[\alpha]_D$ +41° while the 3-methylnonanoic acid had $[\alpha]_D$ +5.25°. Assuming 74% optical purity of the acid, this is corrected to be +7.1° for a maximum rotation. Thus, the acid derived from racemic 2-iodooctane and **1** had an optical purity of only 34% and suggested to us that the reported value was too low. This experiment tends to validate the technique reported here and should allow prediction of maximum rotation in these classes of compounds.

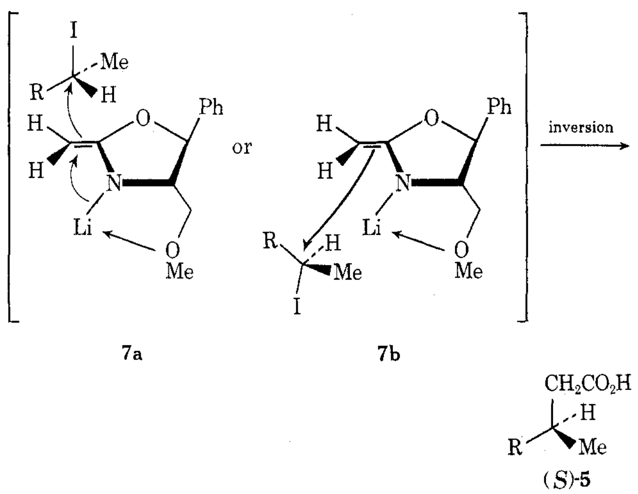
Reaction of **1** with a larger excess of racemic halide (6–8 equiv) gave recovered iodides (iodobutane and iodooctane in 6 and 9% optical purity, respectively) and increased optical purity of the corresponding acids (39–40%). Thus, the asymmetric yields of 3-methylalkanoic acids can be increased to even higher levels by employing these conditions.

Since the iodides **4** are recovered with the *R* enantiomer in excess, the transition state during alkylation must assume the orientation depicted in **6a** or **6b** which preferentially consumes the *S* enantiomer. This approach to the transition state appears to involve a minimum of nonbonded interactions. In contrast, the *R* enantiomer of the iodide generates considerably more interactions as the transition state is approached (**7a** or **7b**). The results of the alkylations are consistent with this view since iodide displacement on the more favorably disposed *S* enantiomer (whose Cahn–Ingold–Prelog sequencing is the same in both the halide and the acid) should proceed with inversion leading to the (*R*)-acids, **5**. The absolute configurations of the acids[5] **5** and the halides[5] **4** are known to be *R*.

via S enantiomer



via R enantiomer



Although only three examples involving kinetic resolution of *sec*-alkyl iodides are reported here, this method indicates that it may now be possible, in addition to predicting maximum rotations, to correlate absolute configurations of halides (or their alcohol precursors) and 3-alkylalkanoic acids (or their derivatives, *e.g.*, alcohols, halides, ketones, etc.) by employing racemic starting materials, provided of course, that the absolute configuration of either the acid or halide is known. We continue to evaluate this useful new tool.

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(3) Prepared using acetonitrile imidate ether as described in ref 1, $[\alpha]^{25}_D$ −113.8° (*c* 10.5, $CHCl_3$). The chiral methoxyamino alcohol was recovered after hydrolysis of **3** and recycled to the starting oxazoline **1**.

(4) Prepared according to Berlak (Table I, ref *c*) from commercial 2-octanol {$[\alpha]_D$ −8.97° (neat)}. The (+)-iodooctane thus obtained had $[\alpha]_D$ +44.07° (neat) which represents 70.4% optical purity (based on $[\alpha]_D$ 62.6°).

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The Degenerate Rearrangement of the Benzo-6,7-bicyclo[3.2.2]nonatrienyl Anion. The Relative Stability of a Benzylic and an Allylic Anion[1]

Summary: The benzo-6,7-bicyclo[3.2.2]nonatrienyl anion undergoes a facile degenerate 7-carbon scrambling detected using ^{13}C nmr techniques; the rearrangement has been used to probe relative anion stabilities.

Sir: It was recently shown that the bicyclo[3.2.2]nonatrienyl anion I undergoes a degenerate rearrangement.[2] We now report that this facile rearrangement provides a convenient method for the determination of relative carbanion stabilities. When a substituent is introduced onto the bicyclo[3.2.2]nonatrienyl anion framework, a new equilibrium is established which reflects the substituent influence on carbanion stability. The benzo group is used here as a substituent to test the relative stabilities of a benzylic and an allylic anion. The literature data on this question are ambiguous.[3,4] The advantages of Stothers' method[5] for determining deuterium location by carbon-13 nmr spectroscopy are also illustrated.