

512-cm⁻¹ bands of about equal intensity (unperturbed **1** has a broad, flat emission presumably involving both the 0,0 and 512-cm⁻¹ bands). However, complexation of Na⁺ causes the 0,0 emission to be about twice the intensity of the 512-cm⁻¹ peak, and the K⁺ and Rb⁺ effects on **1** fall smoothly between the Cs⁺ and Na⁺ extremes. Conformational changes in the C-11,28 region discussed above could affect the 512-cm⁻¹ (and/or the superimposed 510-cm⁻¹) normal coordinate motions²⁰ and thus cause the changes in phosphorescence structure (the same general changes occur in the lower energy emission peaks built on the 1379-cm⁻¹ mode).

Surprisingly, the complexation induced changes in rate constants for excited-state processes² are not correlated with crown ether conformational changes. This is so despite the dependence of the rate for radiationless decay of the triplet (k_{dt}) and S₁-T₁ intersystem crossing (k_{isc}) on vibrational overlap²¹ and the dependence of the fluorescence rate constants (k_f) of naphthalene derivatives on vibronic coupling.²² These observations are important in judging the usefulness of crown ether models like **1** for the study of excited-state perturbation by oriented cations. In the case of crown **1** it seems likely that conformationally independent cation-chromophore interactions are responsible for changes in k_f and other rate constants observed upon complexation. Thus those rate constant changes may give direct indications of the intrinsic properties of excited states and perturbers.

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References and Notes

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- (2) L. R. Sousa and J. M. Larson, *J. Am. Chem. Soc.*, **99**, 307 (1977); a full description has been submitted for publication.
- (3) Examples using crown ethers include (a) D. Live and S. I. Chan, *J. Am. Chem. Soc.*, **98**, 3769 (1976); (b) M.-C. Fedarko, *J. Mag. Reson.*, **12**, 30 (1973). Studies of charge effects involving σ -bond connections are more plentiful and include ref 1b, 1c, and 1f.
- (4) "Titration" curves show a clear bend at the equivalence point, and their shapes indicate that (1:1) complexation is essentially complete when the salt/crown ratio is >2. When complexation is incomplete, shifts caused by an added increment of salt are different for each pair of equivalent carbons and proportional to the shift ultimately observed at full complexation. Lithium salts are evidently not complexed.
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- (6) N. K. Wilson and J. B. Stothers, *J. Mag. Reson.*, **15**, 31 (1974).
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- (9) The INDO program was written by Professor J. F. Harrison and uses the method of J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).
- (10) The +1 and +2 species were generated from lithium and beryllium atoms by setting α s to 10, β s to 10, and G and F to 0.0. The "Li" and "Be" thus generated in calculations of **2** had charges of +0.97 and +1.97, respectively. Other parameters were as described by W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
- (11) D. L. Ward, H. S. Brown, and L. R. Sousa, *Acta Crystallogr., Sect. B*, in press. The complex has the K⁺ on a C₂ axis and centered in the crown ring which has all -O-CH₂CH₂-O- units gauche.
- (12) Agreement would appear even better if the experimental results for Na⁺ and not Cs⁺ were plotted (the C-1,4 experimental +1 value would move up to -1.65 $\Delta\delta$).

- (13) W. J. Hehre, R. W. Taft, and R. D. Topsom, *Prog. Phys. Org. Chem.*, **13**, 159 (1976). Note that the slope associated with Figure 2 is largely determined by the ipso (2,3) and ortho (1,4) carbons where effects in addition to charge density are thought to be important.
- (14) F. A. L. Anet, J. Krane, J. Dale, K. Daavatin, and P. O. Kristiansen, *Acta Chem. Scand.*, **27**, 3395 (1973).
- (15) Field effects on saturated carbons are not necessarily simple (see ref 1a and 1d), and, without extensive model studies, detailed knowledge of conformation cannot be easily extracted.
- (16) This assignment is also based on the similarity of the chemical shift of the 11 (and 28) carbon in **1** and the corresponding carbons in the bis(methoxymethyl) ether **2** (see note 5c).
- (17) The field effect of a monopole centered in the crown ring (stretched or contracted as required) meets this criterion.
- (18) Crown folding may be the cause of the difference in the naphthalene 1,4-carbon shift observed when **1** complexes Na⁺, though it is not clear what set of conformational changes affecting carbons 1 and 4 would leave the shifts for carbons 2 and 3 "normal". With Ca²⁺ complexation the C-1,4 upfield shift is large enough to counteract the charge-related downfield shift shown by Ba²⁺. The 2,3 shift may also be influenced toward higher field by Ca²⁺-induced conformational shifts and/or a change in average Ca²⁺ position. See E. L. Eliel et al., *J. Am. Chem. Soc.*, **97**, 322 (1975).
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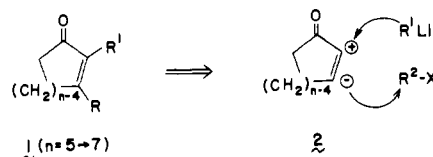
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A Versatile and Expedient Synthesis of α,β -Unsaturated Ketones. Utilization of the β -Epoxy Sulfone Functional Group as the Enone Progenitor

Sir:

In connection with our synthetic program we required expedient methodology for the preparation of a variety of α,β -disubstituted cycloalkenones **1**. We specifically desired a strategy which would afford products formally derived from the doubly charge-inverted ynone synthon **2**^{1,2} such that R¹ and R² could be introduced sequentially as an organolithium reagent and an alkylating agent, respectively.



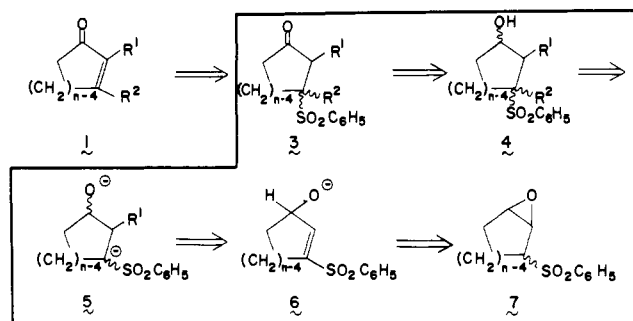
Since β -keto sulfones have recently been shown to be excellent enone precursors (**3** \rightarrow **1**),³ and, also, since oxidation of an alcohol to a ketone (**4** \rightarrow **3**) should pose no severe limitations, we selected dianion **5** as the target molecule for our synthetic efforts. C-Alkylation of **5** would be conceptually expected to produce β -hydroxy sulfone **4** after protonation. Dianion **5** is the formal result of a Michael-type reaction of an organolithium reagent with γ -oxido α,β -unsaturated sulfone **6**, a species which should in turn be produced by base-catalyzed β -elimination of β -epoxy sulfone **7**. The entire five-reaction sequence (**7** \rightarrow **1**) should furthermore be achievable in a "one-" or "two-pot" chemical operation without any purification of intermediates!

We are exceptionally pleased to report that this is indeed the case. Reaction of β -epoxy sulfone **7a**^{4,5} (THF, 0.25 M, -78 °C) with 1 equiv of phenyllithium produces γ -oxido α,β -un-

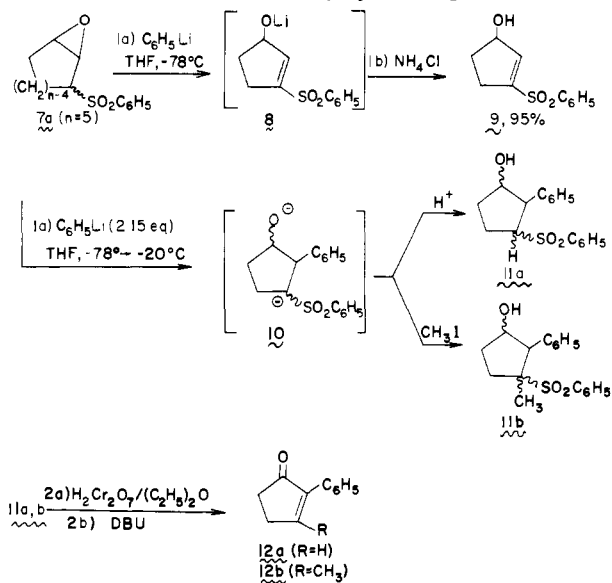
Table I

Epoxy sulfone	R ¹	R ²	Overall % yield (from 7) ^a
7a (n = 5)	C ₆ H ₅	H	12a, 71
7a	C ₆ H ₅	CH ₃	12b, 89
7a	C ₆ H ₅	CH ₂ C ₆ H ₅	12c, 80
7a	C ₆ H ₅	CH ₂ CH=CH ₂	12d, 70 ^b
7a	C ₆ H ₅	(CH ₂) ₃ OSi(CH ₃) ₂ C(CH ₃) ₃	12e, 60 ^c
7a	nC ₄ H ₉	H	12f, 60
7a	nC ₄ H ₉	CH ₃	12g, 66
7a	CH ₃	H	12h, 40 ^d
7a	CH ₃	CH ₃	12i, 63
7b (n = 6)	C ₆ H ₅	H	12j, 45
7b	C ₆ H ₅	CH ₃	12k, 45
7b	nC ₄ H ₉	H	12l, 56
7b	nC ₄ H ₉	CH ₃	12m, 44
7c (n = 7)	C ₆ H ₅	H	12n, 89
7c	C ₆ H ₅	CH ₃	12o, 70
7c	nC ₄ H ₉	H	12p, 57
7c	nC ₄ H ₉	CH ₃	12q, 46 ^e

^a Yields not optimized. ^b DBU elimination run at 0 °C to prevent olefin isomerization. ^c Oxidation (step 1c) via CrO₃·C₅H₅N.⁹ ^d Mechanical losses associated with product volatility. ^e DBU elimination run at 100 °C, 8h.



saturated sulfone **8**,⁶ which yields γ -hydroxy sulfone **9**^{5,7} (95%) upon quenching with saturated ammonium chloride. Repetition of the above experiment with 2 equiv of phenyllithium⁶ (−20 to −30 °C), followed by quenching with saturated



aqueous ammonium chloride or methyl iodide, produces hydroxy sulfones **11a** and **11b**, respectively (as a mixture of diastereomers). Two-phase oxidation^{8,9} of crude hydroxy sulfones **11a** and **11b** (H₂Cr₂O₇/ether), followed by elimination of the β -sulfonyl moiety (most often done by directly treating the water-washed ether phase of the oxidation reaction with 1.5 equiv of diazabicycloundecene, DBU), generates enones **12a** and **12b**. Purification of enones **12a** and **12b** (and subsequent examples) is simply effected by filtration through a short plug of silica gel to remove small quantities of polar impurities and/or biphenyl. The overall yields⁷ of **12a** and **12b** from **7a** are 71 and 89%, respectively.

Repetition of the sequence with a variety of simple substrates (**7a–c**), alkyllithium reagents,¹⁰ and electrophilic species demonstrates considerable generality for this strategy^{11,12,13} (Table I).

Acknowledgment. This investigation was supported by Grant No. CA-19689-01, awarded by The National Cancer Institute, DHEW.

References and Notes

- For an excellent discussion of polarity inversion operations, see D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974).
- Although the working equivalent of **2** has not previously been reported, synthons for singly charge-inverted operators at either the α^{2a-c} and $\beta^{1,3}$ carbons are known. (a) P. L. Fuchs, *J. Org. Chem.*, **41**, 2935 (1976); (b) E. J. Corey, L. S. Melvin, Jr., and M. F. Haslinger, *Tetrahedron Lett.*, 3117 (1975); (c) G. Stork and A. Ponnas, *J. Org. Chem.*, **41**, 3937 (1976).
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- Preparation of **7a**: 3-Thiophenylcyclopentene^{4a} (prepared by addition (−78 → +25 °C) of 3-chlorocyclopentene^{4b} to sodium thiophenoxide in THF (75%) (68.6 g, 390 mmol) is added dropwise to a cooled (0 °C) solution of 40% peracetic acid (153 mL, 1.56 mol) buffered by sodium acetate (6 g). The addition is maintained at such a rate to ensure a constant exotherm, but not exceeding 10 °C; upon complete addition, the reaction mixture is heated for 42 h at 50 °C. (Additional peracid is added (0.1–0.2 mol) at 24 h if starch-iodide paper indicates the absence of peracid.) The reaction mixture is diluted with 20% Na₂SO₃ (100 mL), neutralized at 0 °C with 20% NaOH, and extracted with 1 × 700 mL of CH₂Cl₂ and 2 × 200 mL of CH₂Cl₂. The combined organic portions are washed with 2 × 200 mL of 10% NaHCO₃ and 1 × 200 mL of H₂O, dried (MgSO₄), and concentrated by rotary evaporation. After removal of solvents, the white crystalline epoxy sulfone is recrystallized from Et₂O/hexane at −20 °C (**7a**,⁵ 74.3 g, 85%⁷ as a mixture of diastereomers, mp 53–57 °C). Preparation of **7b**: 3-Thiophenylcyclohexene^{4b} (0.1 mol) is similarly converted to **7b** via room temperature reaction with 3 equiv of *m*-chloroperoxybenzoic acid (MCPBA) in CH₂Cl₂ (91% yield⁷). For larger scale (1–2 mol) preparations it is more economical to first oxidize the allyl sulfide to the allyl sulfone with 2 equiv of peracetic acid as above, followed by epoxidation at 50 °C with MCPBA (**7b**,⁵ crystallized from Et₂O/hexane, mp 54–56 °C, as a mixture of diastereomers). Synthesis of **7b** by a 3-equiv peracetic acid oxidation procedure (50 °C, 48 h) produces a mixture (>80% **7b**) which is exceedingly difficult to crystallize and far less convenient than the two-stage process detailed above. Preparation of **7c**: **7c** (0.1 mol) was prepared from allyl sulfide, using MCPBA oxidation (94%⁷ mp 60–63 °C, as a mixture of diastereomers). (a) D. A. Evans, G. C. Andrews, T. J. Fujimoto, and D. Wells, *Tetrahedron Lett.*, 1385 (1973). (b) R. B. Moffett, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 238.
- The structure of this compound is assigned on the basis of IR, ¹H NMR and/or ¹³C NMR, and elemental analysis or exact mass measurements.
- Monoanion **8** may also be conveniently generated by reaction of **7a** with 0.95 equiv of methylithium (THF, −78 °C). This is important in those cases where the eventual R¹ group (of **1**) is too valuable to also be employed as base for γ -oxido sulfone generation (**7** → **8**). For example, conversion of **7a** to **11b** can also be smoothly effected (93% overall) by sequential reaction of **7a** with methylithium (0.95 equiv), followed by phenyllithium (1.15 equiv), and alkylation with methyl iodide. Under these conditions <2% methyl addition was observed (as assayed by VPC after oxidation of **11b** to enone **12b**). Use of *n*-butyllithium was less successful in this regard (\approx 7% *n*-butyl addition at −78 °C).
- ⁷Yields refer to isolated material of >95% purity.
- H. C. Brown, C. P. Garg, and K. T. Liu, *J. Org. Chem.*, **36**, 387 (1971).
- Both the chromium trioxide-pyridine^{9a} and pyridinium chlorochromate^{9b} reagents also effect the desired oxidation; however, owing to mechanical losses, the yields are usually 10–15% lower. In certain instances (such as **12c**) these less acidic conditions will undoubtedly prove advantageous. (a) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968). (b) E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 2467 (1975).
- Since **12a** could be prepared in 75% yield from **7a** using phenylmagnesium bromide in place of phenyllithium, Grignard reagents also appear to work well in this reaction.
- General procedure for conversion of β -epoxy sulfones **7a–c** to cycloalk-enones **12**: β -Epoxy sulfone **7** (5.0 mmol) is dissolved in THF (25 mL, room

temperature) and the solution is cooled to -78°C . To this solution is added dropwise the organolithium reagent (10.75 mmol) maintaining temperature below -50°C . The reaction is slowly warmed while monitoring (TLC: SiO_2 , 40% $\text{Et}_2\text{O}/\text{CHCl}_3$) the disappearance of β -hydroxy α,β -unsaturated sulfone (**9**) and the appearance of the conjugate addition product (**10**). The following temperatures and times are typical for the conjugate addition reaction: *n*-butyllithium, $-78 \rightarrow 50^{\circ}\text{C}$, 1–2 h; phenyllithium and methyl-lithium, $-78 \rightarrow -25^{\circ}\text{C}$, 1–2 h. After the addition is complete the reaction mixture is cooled to -60°C , the appropriate alkylating agent is added (6.0–7.5 mmol), and the solution is allowed to warm to room temperature. The THF is removed in vacuo and the reaction mixture is partitioned between ether and saturated ammonium chloride solution. The ether phase (100–200 mL) is transferred to a separate reaction vessel and allowed to react with chromic acid solution⁸ (2.0 M, 30 mmol) at room temperature for 1–2 h with vigorous stirring. After standard extraction⁹ of the ether phase, diazabicycloundecene (10 mmol) is added to the separatory funnel and is occasionally shaken. The elimination reaction is usually complete (TLC) within 0.5–1 h at room temperature. The ether phase is washed with $2 \times 5\%$ HCl, $2 \times$ saturated NaHCO_3 , dried over MgSO_4 , and evaporated in vacuo. The crude reaction product may be further purified by filtration through a short plug of SiO_2 (20% THF/hexane, 100–200 mL) to provide pure enones in the overall yields⁷ indicated in Table I.

- (12) The use of this reaction in more highly functionalized systems is currently under active investigation.
- (13) The key to this strategy is the organolithium (Grignard¹¹) conjugate addition reaction.¹⁴ The synthesis was designed to use the γ -oxido group of unsaturated sulfone **8** as a "protecting group" to prevent unwanted γ -proton abstraction by the organometallic reagent. We were consequently surprised to find that reaction of phenyllithium or *n*-butyllithium (1.2 equiv, inverse addition) with 1-phenylsulfonylcyclopentene¹⁵ or 1-phenylsulfonylcyclohexene¹⁵ smoothly ($>80\%$) provides the conjugate-addition products (as a mixture of diastereomers) with only a trace of γ -proton abstraction.¹²
- (14) Posner reports that organocuprate reagents also undergo conjugate addition reactions to unsaturated sulfones (under more forcing conditions): G. H. Posner and D. J. Brunelle, *J. Org. Chem.*, **38**, 2747 (1973).
- (15) P. B. Hopkins and P. L. Fuchs, *J. Org. Chem.*, in press.
- (16) Graduate Research Associate.
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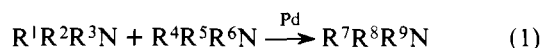
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Palladium Catalyzed Amine Exchange Reaction of Tertiary Amines. Insertion of Palladium(0) into Carbon-Hydrogen Bonds

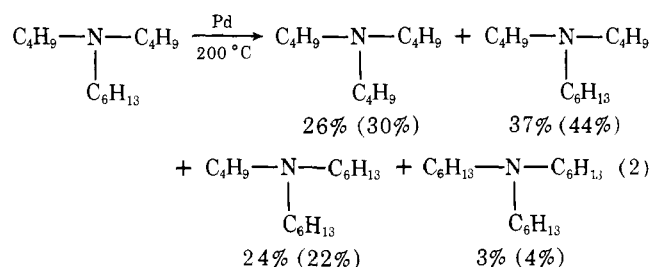
Sir:

Interaction between a carbon-hydrogen bond and a metal center in both heterogeneous¹ and homogeneous systems² are currently the subject of much study. We here wish to report a novel palladium catalyzed exchange reaction of tertiary amines, whose initial step seems to be an insertion of palladium into a carbon-hydrogen bond adjacent to the nitrogen, leading to a highly active intermediate complex of an iminium ion, to which much attention has been paid quite recently.³

The palladium catalyzed amine exchange reaction of tertiary amines occurs at 200°C , highly efficiently, as depicted below.



This process may provide a convenient method for the synthesis of unsymmetrical tertiary amines because of high efficiency, simplicity, and facile isolation of the desired products by distillation. In a typical case, a mixture of dibutylhexylamine and a catalytic amount of palladium black was reacted in an autoclave at 200°C for 16 h. Filtration of the palladium catalyst followed by distillation gave a mixture of four tertiary amines: tributylamine (26%), dibutylhexylamine (37%), butyldihexylamine (24%), and trihexylamine (3%)⁴ (entry 2 in Table I). If tertiary amine $\text{R}^1_2\text{R}^2\text{N}$, for example, is converted into a mixture of tertiary amines whose alkyl groups (R^1 and R^2) are distributed statistically, four tertiary amines, R^1_3N , $\text{R}^1_2\text{R}^2\text{N}$, $\text{R}^1\text{R}^2\text{R}^3\text{N}$, and R^2_3N could be formed, and the product distribution of $\text{R}^1_m\text{R}^2_{3-m}\text{N}$ ($m = 0, 1, 2, 3$) can be calculated by the equation of $\lim_{n \rightarrow \infty} (2n C_m)(n C_{3-m})/3n C_3$ at equilibrium. Surprisingly, the product yields observed are consistent with those calculated by using the equation, as indicated in the parentheses in eq 2. Moreover, when an equimolar mixture of



tributylamine and trihexylamine was reacted under these conditions,⁵ tributylamine (16%), trihexylamine (16%), dibutylhexylamine (31%), and butyldihexylamine (31%) were obtained, and their yields are also consistent with those calculated statistically, 13, 13, 37, and 37%, respectively (entry 4). Other examples⁶ of the exchange reactions of tertiary amines are shown in Table I.

These reactions can be rationalized by assuming Scheme I, in which palladium coordinates to nitrogen and undergoes insertion into the adjacent C-H bond to give **2**, which then comes to rapid equilibrium with a key intermediate, an iminium ion complex (**3**). In support of insertion of palladium into the C-H bond of the α position of tertiary amines, recovered (*S*)-(+)-*N,N*-dimethyl-*sec*-butylamine (**10**) was found to have $\sim 15\%$ of the optical rotation of the starting amine upon

Table I. Product Yields Obtained by Palladium Catalyzed Exchange Reaction of Tertiary Amines (Eq 1)^a

Entry	$\text{NR}^1\text{R}^2\text{R}^3$			$\text{NR}^4\text{R}^5\text{R}^6$			$\text{NR}^7\text{R}^8\text{R}^9$ ^b (% yield, ^c % calculated yield ^d)							
	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^7	R^8	R^9		
1	CH ₃	C ₄ H ₉	C ₄ H ₉				CH ₃	CH ₃	CH ₃	(-, 4)	CH ₃	CH ₃	C ₄ H ₉	(18, 22)
							CH ₃	C ₄ H ₉	C ₄ H ₉	(48, 44)	C ₄ H ₉	C ₄ H ₉	C ₄ H ₉	(25, 30)
2	C ₄ H ₉	C ₄ H ₉	C ₆ H ₁₃				C ₄ H ₉	C ₄ H ₉	C ₄ H ₉	(26, 30)	C ₄ H ₉	C ₄ H ₉	C ₆ H ₁₃	(37, 44)
							C ₄ H ₉	C ₆ H ₁₃	C ₆ H ₁₃	(24, 22)	C ₆ H ₁₃	C ₆ H ₁₃	C ₆ H ₁₃	(3, 4)
3	C ₃ H ₇	C ₄ H ₉	C ₆ H ₁₃				C ₃ H ₇	C ₃ H ₇	C ₃ H ₇	(3, 4)	C ₃ H ₇	C ₃ H ₇	C ₄ H ₉	(10, 11)
							C ₃ H ₇	C ₄ H ₉	C ₄ H ₉	(10, 11)	C ₄ H ₉	C ₄ H ₉	C ₄ H ₉	(3, 4)
							C ₃ H ₇	C ₃ H ₇	C ₆ H ₁₃	(10, 11)	C ₃ H ₇	C ₄ H ₉	C ₆ H ₁₃	(29, 22)
							C ₄ H ₉	C ₄ H ₉	C ₆ H ₁₃	(10, 11)	C ₃ H ₇	C ₆ H ₁₃	C ₆ H ₁₃	(10, 11)
							C ₄ H ₉	C ₆ H ₁₃	C ₆ H ₁₃	(10, 11)	C ₆ H ₁₃	C ₆ H ₁₃	C ₆ H ₁₃	(3, 4)
4	C ₄ H ₉	C ₄ H ₉	C ₄ H ₉	C ₆ H ₁₃	C ₆ H ₁₃	C ₆ H ₁₃	C ₄ H ₉	C ₄ H ₉	C ₄ H ₉	(16, 13)	C ₄ H ₉	C ₄ H ₉	C ₆ H ₁₃	(31, 37)
							C ₄ H ₉	C ₆ H ₁₃	C ₆ H ₁₃	(31, 37)	C ₆ H ₁₃	C ₆ H ₁₃	C ₆ H ₁₃	(16, 13)
5	C ₄ H ₉	C ₄ H ₉	C ₄ H ₉	C ₈ H ₁₇	C ₈ H ₁₇	C ₈ H ₁₇	C ₄ H ₉	C ₄ H ₉	C ₄ H ₉	(18, 13)	C ₄ H ₉	C ₄ H ₉	C ₈ H ₁₇	(30, 37)
							C ₄ H ₉	C ₄ H ₁₇	C ₈ H ₁₇	(30, 37)	C ₈ H ₁₇	C ₈ H ₁₇	C ₈ H ₁₇	(18, 13)

^a Reaction was carried out at 200°C for 16 h. ^b Satisfactory IR and ¹H NMR was obtained for all compounds. ^c Yield is based upon starting amines. All yields are determined by GLC analysis vs. eicosane or tridecane as an internal standard. ^d Yield in italics is calculated based upon the statistical calculation at complete equilibrium.