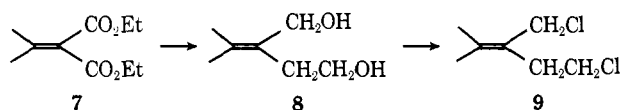


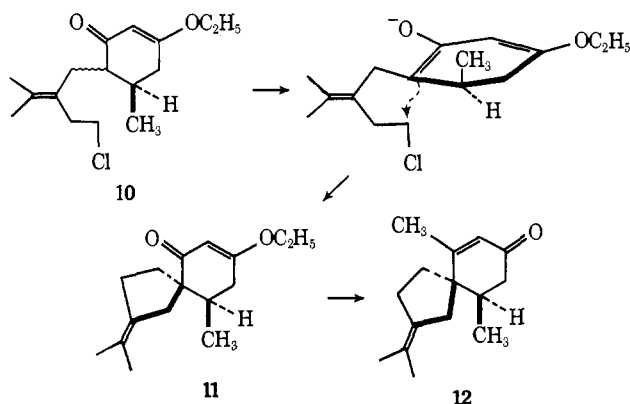
alkyl halide **9** required for the spiroannulation of **5** was synthesized from diethylisopropylidene succinate (**7**)⁵ by reduction with lithium aluminum ethoxy hydride (~2 mol, ether at room temperature) to the glycol **8** (90% yield, bp 99–107° (0.15–0.2 mm); mp ~35°; *m/e* 130.0973; nmr δ 1.7 (3 H, s), 1.8 (3 H, s), 2.4 (2 H, t), 3.63 (2 H, t), 4.1 (2 H, s), 4.4 ppm (2 H, s)) and conversion of **8** into the corresponding dichloride **9**. This last conversion was, not unexpectedly, difficult (cyclic ether formation). It was finally achieved⁶ by slow addition (N₂) of a solution of the dilithium salt of **8** (methyl-lithium, triphenylmethane indicator, 75:50 ether–hexamethylphosphoramide) into an ether solution (–35–50°) of 2.2 equiv of methanesulfonyl chloride and 7 equiv of lithium chloride. Further addition of hexamethylphosphoramide (final ratio ether–hexamethylphosphoramide 2.2:1), followed by 45 hr at room temperature, gave the required dichloride **9** in 35% yield



(bp 88–90° (8 mm); nmr δ 4.21 (2 H, s), 3.52 (2 H, t), 2.62 (2 H, t), 1.81 (3 H, s), and 1.76 ppm (3 H, s)).

Spiroannulation of **5** with **9** was carried out by allowing the lithium enolate of **5** (from **5** in tetrahydrofuran containing 1 equiv of hexamethylphosphoramide and 1 equiv of lithium diisopropylamide in tetrahydrofuran at –78°) to react with the dichloride **9** (30% excess) for 13 hr at room temperature. Addition of 2 additional equiv of lithium diisopropylamide, followed by 30 hr at room temperature, gave after chromatography (silica gel, benzene) in ~45% yield the annelated enol ether **11** (one spot on silica gel, 15:85 ethyl acetate–benzene, *m/e* 248.1773; ir 6.01, 6.17 μ ; nmr δ 5.25 (1 H, b, *J* ~ 2 Hz), 3.85 (2 H, q), 1.63 (6 H, s (b)), 1.37 (3 H, t), 1.8–2.9 (9 H, m), 0.98 ppm (3 H, d).

The stereochemistry of the spiroannelated enol ether **11** was anticipated to be as shown because the first alkylation would obviously involve the allylic halide to give **10**. The subsequent enolate ion geometry then



forces the ring methyl into an axial conformation⁷ and one would expect completion of the ring trans to that methyl. The correctness of this assumption was easily

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checked by transformation to (\pm)- β -vetivone (**12**). Addition of methyl lithium (1.2 equiv) to **11** in ether at 0°, followed by 12 hr at room temperature and treatment with 1 *N* HCl at room temperature for 3 hr, gave, in ~60% yield after chromatography (silica gel, benzene), (\pm)-vetivone (**12**), mp 40–44° (lit.⁴ mp 43.5–46°), homogeneous on silica gel (15:85 ethyl acetate–benzene). The identity of the substance was established by glc comparison with natural material, by the identity of the infrared, mass, and 220-Hz nmr spectra with those of authentic natural material. In addition, the melting point of the (\pm)-2,4-dinitrophenylhydrazone of our synthetic material gave no depression with the authentic \pm derivative of the same melting point.^{8–10}

(8) We wish to thank Professor Marshall for his kindness in providing us with the 2,4-dinitrophenylhydrazone of his synthetic material.

(9) We thank Professor P. M. McCurry, Jr., for making available to us samples of pure natural β -vetivone and for carrying out the glc comparisons of the synthetic and natural materials.

(10) We thank the National Science Foundation for their support of this work.

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Received February 6, 1973

α -Lactams. IX. Conjugation Effects of the α -Lactam Ring

Sir:

The previously reported ultraviolet absorption maxima of aliphatic α -lactams at 250 nm has been explained by considering a dipolar, delocalized amide type of structure for the excited state.¹ This resonance form of α -lactams is supported by the fact that these compounds have been successfully O-alkylated.²

While observing the ultraviolet spectra of C-3 phenyl-substituted α -lactams in pentane solution a new property of this structure was discovered—a bathochromic shift of the primary benzene band which we suggest is due to conjugative interaction of the α -lactam ring with the phenyl ring. 1-*tert*-Butyl-3-phenylaziridinone (**1**)³ (λ_{max} (pentane) 226 nm (log ϵ ~4.0)) and 1-*tert*-butyl-3-(*p*-trifluoromethyl)phenylaziridinone (**2**) (λ_{max} (pentane) 237 nm (log ϵ ~4.0)) exhibit benzene bands considerably shifted from the corresponding absorptions of model ring-opened compounds **3** (λ_{max} (pentane) 207 nm (log ϵ ~3.9)) and **4** (λ_{max} (pentane) 208 nm (log ϵ ~3.9)), Figures 1 and 2. This phenomenon is analogous to the well-documented bathochromic shift observed with phenylcyclopropanes where the effect of the ring is intermediate to that of straight chain and olefinic substituents.^{4,5} In the present case the absorption of the α -lactam carbonyl at 250 nm could not be distinguished from aromatic absorptions appearing in the same region.

The aziridinones **1** and **2** are prepared using a modification of our general procedure for synthesis of α -

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(5) R. C. Hahn, P. H. Howard, S.-M. Kong, G. A. Lorenzo, and N. L. Miller, *J. Amer. Chem. Soc.*, **91**, 3558 (1969).

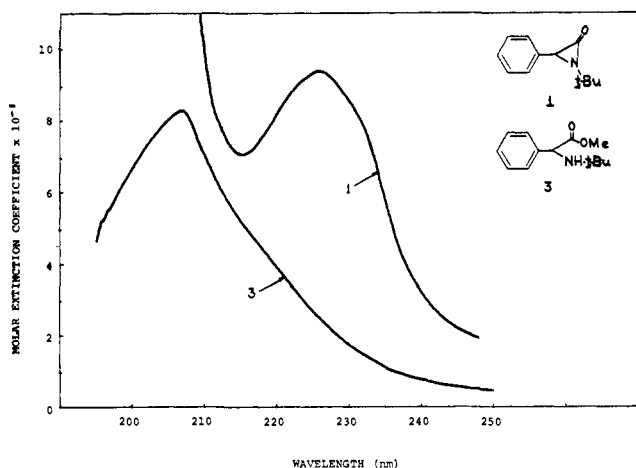
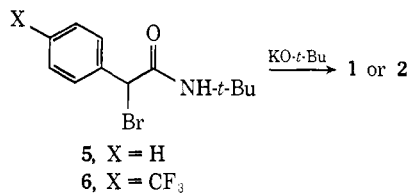


Figure 1. Uv spectra of 1-*tert*-butyl-3-phenylaziridinone (1) and methyl 2-*tert*-butylamino-2-phenylacetate (3).

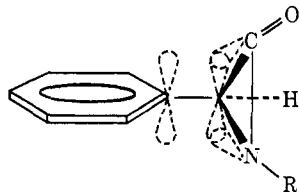
lactams.⁶ The corresponding *N*-*tert*-butyl-2-bromo-phenylacetamide **5** or **6**⁷ (1 equiv) is treated with po-



tassium *tert*-butoxide (1 equiv) in diethyl ether for 30 min at a reaction temperature maintained between -40 and -50° . The reaction mixture is removed through a syphon under nitrogen pressure and filtered into a flask cooled in Dry Ice. After removal of the solvents under reduced pressure at 0° , the residue, a yellow oil, is dissolved in pentane and cooled in Dry Ice, and the precipitate is separated by centrifugation. Concentration of the supernatant liquid followed by distillation in a molecular still at 50 – 60° (0.003 mm) gives the α -lactams **1** and **2** in 23–35% yield.^{8,9}

The open-chain analogs **3** and **4** are obtained by treating a stirred pentane solution of the corresponding α -lactam (1 equiv) with sodium methoxide (3 equiv) for 3 hr. Pure amino esters are isolated following aqueous work-up and preparative gas chromatography.¹⁰

The bathochromic shift observed in the present study presumably arises through a conjugative interaction of the aromatic π system with the α -lactam ring bonds similar to that illustrated, although experiments with



(6) J. C. Sheehan and J. H. Beeson, *J. Amer. Chem. Soc.*, **89**, 362 (1967).

(7) The starting amides **6** and **7** were prepared by the procedure described in ref 6.

(8) The spectroscopic yield of **2** in the reaction solution was 64.5% ($\pm 6\%$) based on a plot of infrared absorbances vs. known concentrations of **2**.

(9) The structures of the new compounds **2**, **3**, **4**, and **6** are consistent with elemental analyses, mass spectra, and nmr and infrared spectra.

(10) 32 cm \times 0.4 cm 20% Silicone-200 on Chromosorb P at 155° .

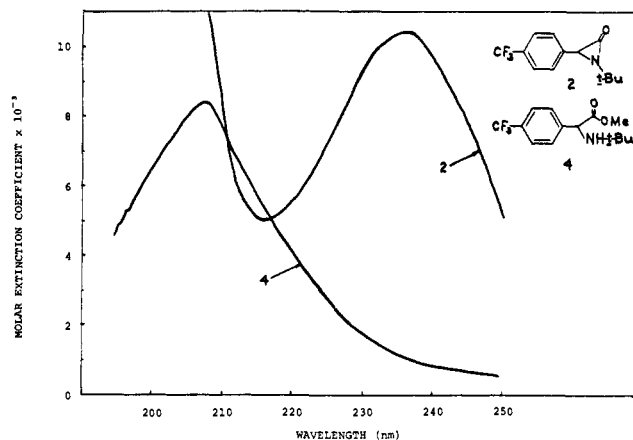


Figure 2. Uv spectra of 1-*tert*-butyl-3-(*p*-trifluoromethyl)phenylaziridinone (2) and methyl 2-*tert*-butylamino-2-(*p*-trifluoromethyl)phenylacetate (4).

phenylcyclopropyl analogs indicate a specific geometry is not necessary.⁵ The trifluoromethyl group of **2** causes an increased and intensified bathochromic shift as expected for a para electron-withdrawing substituent. In general, substituents β to the aromatic ring exhibit no observable effect on the ultraviolet spectrum which appears to be the case for the carbonyl group and the nitrogen atom of the α -lactam ring since the absorption maxima of **1** is very similar to that of phenylcyclopropane (λ_{max} (pentane) 226 nm ($\log \epsilon$ 3.9)).

Acknowledgment. We gratefully acknowledge financial support from the Department of Chemistry for one of us (R. R. K.) in the form of the James Flack Norris Fellowship (1969–1970) and the continued support of the Sloan Basic Research Fund.

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Received January 8, 1973

Reaction of Deuterium Chloride with *cis*- and *trans*- β -Trimethylsilylstyrene

Sir:

While the reactions of aryltrimethylsilanes with electrophiles have been extensively studied,¹ the reactions of vinylsilanes with electrophiles have been examined in much less detail.² The reaction of β -trimethylsilylstyrene with acid was reported to yield styrene almost 20 years ago.³ We have been concerned with the mechanism of this reaction since we have found that it possesses an unusually high degree of stereospecificity for what must be a complex ionic reaction. Specifically we find that *trans*- β -trimethylsilylstyrene⁴ reacts with either DCl or DBr in dry acetonitrile at reflux to yield virtually only *trans*- β -deuteriostyrene. Similarly *cis*- β -trimethylsilylstyrene⁴ yields equally pure *cis*- β -deuteriostyrene.

(1) C. Eaborn and R. W. Bott, "Organometallic Compounds of the Group IV Elements," Vol. I, A. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, Chapter 2, pp 407–435.

(2) C. Eaborn and R. W. Bott in ref 1, pp 392–395.

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(4) D. Seyferth, L. G. Vaughan, and R. Suzuki, *J. Organometal. Chem.*, **1**, 437 (1964).