OMe[27] indicates much freer rotation about ϕ and ψ in this molecule than in Ac-Ala-NHMe. A Boltzmann distribution over the conformational map for Ac-Ala-OMe would give less weight to the combination of ϕ and ψ attributed to the "extended helix"[10,11] than is the case in Ac-Ala-NHMe.

The results reported here demonstrate that a small positive circular dichroism, which is sensitive to temperature and to the presence of salts, can be observed in peptides where the side chain is simply a methyl group and in a structure as small as Ac-Ala-OMe or Ac-Ala-NHMe. These effects cannot arise from the electrostatic interaction of charged side chains nor can they be due to an "extended helix." The temperature effects on the circular dichroism must instead reflect an increasing population of the higher energy regions of the conformational maps as the temperature increases. Calcium chloride and sodium perchlorate, as well as certain other salts, are known to affect the conformational properties of a wide variety of polypeptides.[3] The basic effect, as detected by circular dichroism, is also operative in very small molecules and can perhaps more easily be understood by studying small peptides rather than polypeptides.

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(27) W. L. Mattice, unpublished results.

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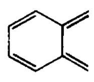
Photochemical Preparation of *o*-Xylylene from 1,4-Dihydrophthalazine in Rigid Glass[1]

Sir:

o-Xylylene (**1**) has evoked intense theoretical[2,3] and experimental[4-14] interest. While direct observations of substituted *o*-xylylenes of varying stabilities have succeeded,[6] evidence for **1** itself is only indirect (a stable metal complex is known[7]). The presence of **1** as an intermediate has been inferred from the nature of the products of trapping[8-10] or self-trapping reactions. The latter give **2**, **3**, **4**, and *o*-xylene. Some reactions which presumably proceed *via* **1** are oxidation[11] of **5** at 0° (**5** → **6** → **1**), thermal decompositions of **7**[9,10,12] and **8**,[13] and uv irradiation[14] of **9**.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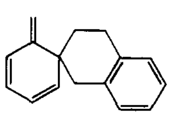
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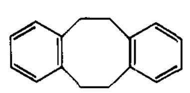
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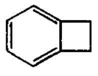
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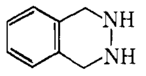

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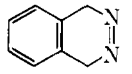

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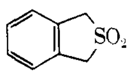

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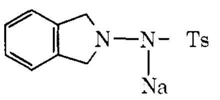

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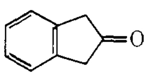

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Our interest in **1** was aroused by work on related hydrocarbons[15] and by studies of the electronic states of biradicals and of photochemical singlet–triplet reactivity differences.[16] This prompted us to search for biradicals whose lowest excited singlet (S_1) and triplet (T_1) states would have the same orbital occupancy; yet, S_1 could be shown to prefer a "tight" geometry and T_1 a "loose" one.[16]

In view of the reactivity of **1** matrix isolation techniques appeared appropriate. We now report a photochemical synthesis of **1** in rigid glass from the previously unreported **6** and some spectral properties of both. Pure **6** is a white powder and was prepared by oxidation of a basic (MeOK or KOH) methanolic solution of **5** at *ca.* −90° with *t*-BuOCl, evaporation of methanol (−78°, 5 × 10^{-6} Torr), and chromatography of the residue on a silica gel column at −80°[17] (C_3H_8 − Me_2O): pmr in acetone-d_6 (−70°) singlets at τ 4.96 and 2.59, equal integrated intensities (*cf.* τ 5.15 for the methylene protons in 1,1′-diphenylazomethane[18] and τ 4.2 in 1,4-dihydronaphtho[1,8-*d*,*e*][1,2]diazepine[11]); uv in Et_2O (−100°) a broad band, λ_{max} 358 nm, ϵ_{max} $\sim 10^2$ (-N=N-), sharp peaks, λ_{max} 265 and 271 nm, ϵ_{max} $\sim 10^3$ (aromatic). Above −40°, the uv and pmr spectra of **6** disappeared, N_2 was evolved, and the known spectra[4] of **2** appeared (preliminary results at −40 to −60° give first-order kinetics, $\Delta H^{\ddagger} = 15 \pm 2$ kcal/mol, $\Delta S^{\ddagger} = -7.5 \pm 3$ eu).

Irradiation (λ 254 nm or λ >345 nm) of **6** at −196° (glassy diethyl ether or EPA) destroyed its characteristic uv absorption and caused rapid formation of a new species (λ_{max} 373 nm, ϵ_{max} >3000). The Franck–Condon forbidden shape of the new band and the vibrational spacing (1400–1500 cm^{-1}) were strongly reminiscent of spectra of related *o*-quinomethides.[19] The photoproduct showed strong fluorescence (spectral shape independent of excitation wavelength, λ_{max} 456

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nm). The excitation spectrum followed the absorption spectrum and was independent of monitoring wavelength. The onsets of absorption and emission coincided; the 0–0 bands were hardly discernible as weak shoulders. No phosphorescence was detected. No triplet epr signal was present after completed irradiation under conditions which easily permitted observation of the half-field triplet signal of ground-state triplets (triphenylene dianion).

Upon strong irradiation (λ >345 nm, 200-W Hg arc) the 373-nm band of the photoproduct was replaced by the uv absorption spectrum[20] of **4**. Conversion was virtually complete after 24 hr. After warm-up, glc analysis confirmed the presence of **4** (two columns, authentic sample[10]).

Melting (*ca.* −150°) of the glassy solution containing the photoproduct from **6** rapidly destroyed the 373-nm uv absorption band and the spectrum[4] of **2** appeared.

Based upon these data the photoproduct from **6** was assigned structure **1**. Further support was obtained by use of additional precursors. Irradiated glassy solutions of **4**,[21] **7**, **8**, and **9** (EPA, −196°, 254-nm light) contained a common species with a uv absorption spectrum as above, except that additional absorbing materials were present. A convincing proof that the photoproduct was the same as obtained from **6** was provided by the identity of emission and excitation spectra in all cases.

Transition energies and intensities calculated in the SCF–CI–PPP approximation using singly excited configurations[22] agreed well with the experimental spectrum. The Franck–Condon forbidden shape of the first band is in accordance with a substantial change of calculated bond orders upon excitation (toward regular hexagon).

Results of additional PPP calculations using up to 150 configurations[23] were similar, except that one of the higher energy transitions acquired partial doubly excited character (*cf.* ref 2) and became approximately degenerate with the first transition. Similar states have been calculated for other polyolefins[24] and probably observed in one case.[25] An observation of a predominantly doubly excited state has also been claimed.[15b]

Energy of vertical excitation from the lowest singlet state S_0 into T_1 calculated using the method and parameters of ref 26 is 8000 cm^{-1} compatible with ref 2 and our epr results indicating that **1** does not have a triplet ground state.[27] The triplet has been predicted[3] to slightly prefer a geometry with one CH_2 group twisted.[28] On the other hand, spectral shape and intensity of fluorescence indicate that S_1 is planar. According to calculations, planar S_1 and T_1 have the same orbital occupancy (HOMO → LUMO excitation) and **1** thus may be an example of the sought type of S_1–T_1 geometry differences.

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[27] Planar **1** in the T_1 state is calculated to distort to an almost regular hexagon. At this geometry, T_1 is predicted to be 5000 cm^{-1} above S_0. The calculated $T_1 \rightarrow T_x$ spectrum of the planar species does not agree with that observed.

[28] The absorption spectrum of the twisted triplet should resemble somewhat the spectrum of the benzyl radical: T. O. Meiggs, L. I. Grossweiner, and S. I. Miller, *J. Amer. Chem. Soc.*, **94**, 7981, 7986 (1972), and references therein. The observed spectrum is dissimilar.

[29] Alfred P. Sloan Foundation Fellow, 1971–1973.

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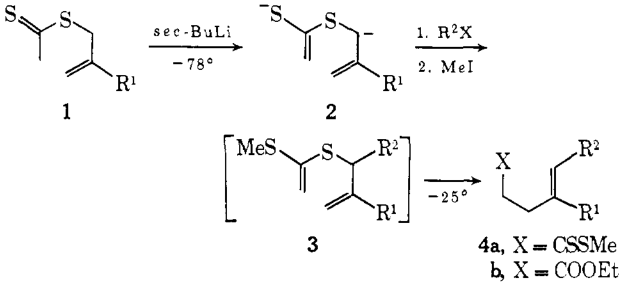
A Simple Stereoselective Version of the Dithio Ester Thio-Claisen Rearrangement Leading to *E*-Trisubstituted Olefinic Bonds

Sir:

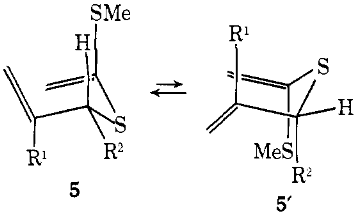
We wish to disclose a version of the dithio ester thio-Claisen rearrangement which is highly stereoselective and can be applied to the synthesis of *E*-trisubstituted double bonds as they appear in many natural products. The method simply involves treatment of the dithio ester **1** with 2 equiv of *sec*-butyllithium followed by successive addition of an alkyl halide and methyl iodide. Evidently a dianion **2** was first formed, which, on stepwise alkylation followed by thio-Claisen rearrangement, affords the dithio ester **4a** *via* the ketene thioacetal **3**.



1 **2** **3**

4a, X = CSSMe
b, X = COOEt

As compared with the current processes for the preparation of the γ,δ-unsaturated acids,[1] this route provides a convenient and versatile method for the introduction of a five-carbon chain terminating in a carboxyl function starting with a simple halide, and the stereoselectivity is also very high. The rigorous stereoselectivity is probably attributable to nonbonding interaction between the thiomethyl and R^2 groups (**5′**) that



5 **5′**

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[1] (a) Ortho ester process: W. S. Johnson, L. Werthemann, W. R. Bartlett, T. J. Brocksom, T. T. Li, D. J. Faulkner, and M. R. Petersen, *J. Amer. Chem. Soc.*, **92**, 741 (1970); (b) enol ester rearrangement: R. E. Ireland and R. H. Mueller, *ibid.*, **94**, 5897 (1972); see also J. E. Baldwin and J. A. Walker, *J. Chem. Soc., Chem. Commun.*, 117 (1973).