

photodetachment occurs with light of wavelength longer than 6400 Å indicates^{3,10} that photodetachment from H⁻ is not being observed on a scale comparable with that of OH⁻.) During the experiment, *f* and *t* in eq 2 remain constant, while the wavelength range is changing. Since the relative spectral intensity of the tungsten bulb decreases at shorter wavelengths,² it is evident that the relative photodetachment cross-section curve for OH⁻ does not fluctuate markedly in the range 6000–4000 Å. This behavior agrees qualitatively with the photodetachment cross section determined by Branscomb.¹² An order of magnitude calculation of the absolute magnitude of the maximum for the cross section is also in accord with Branscomb's value.¹²

A similar study was performed using SH⁻.¹³ In this case photodetachment was not observed for light of wavelength longer than 5840 Å (filters A and B of Figure 1), and photodetachment was observed for more energetic radiation. The results of using the same set of long-wavelength pass filters as before allow a quantitative estimate of the vertical detachment energy of SH⁻ of 2.28 ± 0.15 eV.¹⁴ Since the vibronic ground-state structures of the negative ion SH⁻ and the neutral free radical SH· are similar,¹⁵ the threshold for the photodetachment of SH⁻ occurs at the energy corresponding to the electron affinity¹⁶ of SH·. The value found above agrees within experimental error with that of Steiner, 2.319 ± 0.010 eV.¹⁵ Finally, no photodetachment has been observed with the tungsten light source for Cl⁻, consistent with its known electron affinity of 3.613 ± 0.003 eV.¹⁷

It is now apparent that with beam collimation, more intense light sources, and monochromatic radiation, it should be possible to carry out determinations of photodetachment energies with ease and convenience for a wide variety of negative ions. In favorable cases, this energy can be related directly to the electron affinity, and structural parameters of the ions can be deduced. We expect to report on such determinations shortly.

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(12) L. M. Branscomb, *Phys. Rev.*, **148**, 11 (1966).

(13) Maximum intensities for SH⁻ from H₂S were obtained with an electron beam energy of 2.6 eV (uncorrected).

(14) This estimate is made by assuming that the threshold for photodetachment lies at an energy less than that corresponding to the 10% transmission value of filter C (5130 Å, 2.42 eV) and at an energy greater than that corresponding to the 80% transmission value of filter B (5840 Å, 2.13 eV).

(15) B. Steiner, *J. Chem. Phys.*, **49**, 5097 (1968).

(16) This is true in the case where there is no vibrational excitation and the effects of rotational heating are neglected.

(17) R. S. Berry, C. W. Reimann, and G. N. Spokes, *J. Chem. Phys.*, **37**, 2278 (1962).

(18) Alfred P. Sloan Fellow 1968–1970.

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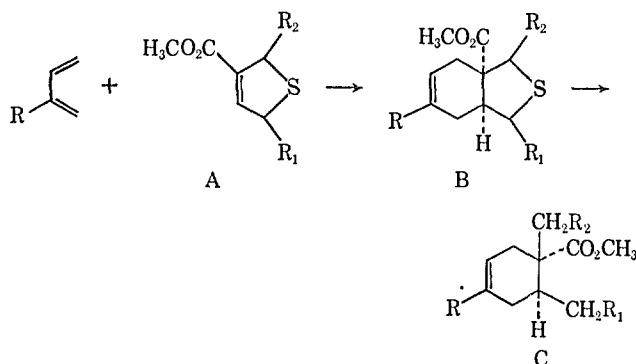
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A New Approach to the Stereospecific Synthesis of Angularly Substituted Polycyclic Systems

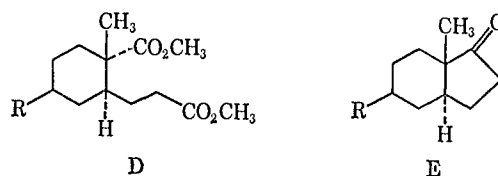
Sir:

The construction of *trans*-fused bicyclic systems has been the object of much effort over the years, especially since the recognition of that structural feature in the C/D hydrindan system of the steroids.¹

We have devised a new approach of some generality for the solution of this synthetic problem. The approach is schematized by the conversion A → C, and it is obvious that when the substituent R₁ is capable of participating in ring formation with the carbalkoxy group (or a function derivable from it) an angularly



substituted *trans* bicyclic system would result, with complete stereospecificity.^{2,3} For instance, should the particular dihydrothiophene be A, R₁ = CH₂CO₂CH₃, R₂ = H, product C would yield after hydrogenation and saponification a (*trans*-2-carboxy)-2-methylcyclohexanepropionic acid (D), the cyclization of which is well known to lead to the 8-methyl-1-hydrindanone system (E).



We now detail the synthesis of the dihydrothiophene A, R₁ = CH₂CO₂CH₃, R₂ = H, and its further transformations along the lines indicated above.

The readily available β-keto ester 1,⁴ from the addition of methyl β-mercaptopropionate and dimethyl maleate followed by cyclization, was reduced most effectively by treatment of its methanol solution with an excess of morpholine–borane⁵ at room temperature until a ferric chloride test became negative (*ca.* 3 hr). Addition of 1.1 equiv of sodium methoxide, removal of solvent, and washing with ether gave the sodium salt of 2,5-dihydro-4-carbomethoxy-2-thiopheneacetic acid, from which was isolated the free acid 2, mp 109.5–110.5° (from ether), λ_{max}^{CHCl₃} 3–4, 5.82, 6.02 μ. Esteri-

(1) Cf. W. S. Johnson, *J. Amer. Chem. Soc.*, **66**, 215 (1944).

(2) The obvious possibility of using homologs of tiglic esters in the Diels–Alder reaction is not feasible because such additions are either unsuccessful or give very low yields.

(3) Clearly, when the groups CH₂R₁ and CH₂R₂ are capable of ring formation a stereospecific construction of *cis* polycyclic systems with an angular carboxyl group would result.

(4) B. R. Baker, M. V. Querry, and A. F. Kadish, *J. Org. Chem.*, **13**, 123 (1948).

(5) From Alfa Inorganics, Inc.

