photodetachment occurs with light of wavelength longer than 6400 Å indicates<sup>3, 10</sup> that photodetachment from H<sup>-</sup> is not being observed on a scale comparable with that of OH<sup>-</sup>.) 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,<sup>2</sup> it is evident that the relative photodetachment cross-section curve for OH<sup>-</sup> does not fluctuate markedly in the range 6000-4000 Å. This behavior agrees qualitatively with the photodetachment cross section determined by Branscomb.<sup>12</sup> 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<sup>-</sup>.<sup>13</sup> 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<sup>-</sup> of 2.28  $\pm$  0.15 eV.<sup>14</sup> Since the vibronic groundstate structures of the negative ion SH<sup>-</sup> and the neutral free radical SH. are similar,15 the threshold for the photodetachment of SH- occurs at the energy corresponding to the electron affinity<sup>16</sup> of SH $\cdot$ . The value found above agrees within experimental error with that of Steiner, 2.319 ± 0.010 eV.<sup>15</sup> Finally, no photodetachment has been observed with the tungsten light source for Cl-, consistent with its known electron affinity of  $3.613 \pm 0.003 \text{ eV}$ .<sup>17</sup>

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<sup>-</sup> from H<sub>2</sub>S 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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## 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.<sup>1</sup>

We have devised a new approach of some generality for the solution of this synthetic problem. The approach is schematized by the conversion  $A \rightarrow C$ , and it is obvious that when the substituent  $R_1$  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.<sup>2,3</sup> For instance, should the particular dihydrothiophene be A,  $R_1 = CH_2CO_2$ - $CH_3$ ,  $R_2 = H$ , 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,  $R_1 = CH_2CO_2CH_3$ ,  $R_2 = H$ , and its further transformations along the lines indicated above.

The readily available  $\beta$ -keto ester 1,<sup>4</sup> from the addition of methyl  $\beta$ -mercaptopropionate and dimethyl maleate followed by cyclization, was reduced most effectively by treatment of its methanol solution with an excess of morpholine-borane<sup>5</sup> 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),  $\lambda_{max}^{CHCl_{4}}$  3-4, 5.82, 6.02  $\mu$ . Esteri-

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<sup>(1)</sup> Cf. W. S. Johnson, J. Amer. Chem. Soc., 66, 215 (1944).

<sup>(2)</sup> 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.

<sup>(3)</sup> Clearly, when the groups  $CH_2R_1$  and  $CH_2R_2$  are capable of ring formation a stereospecific construction of cis polycyclic systems with an angular carboxyl group would result.

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

<sup>(5)</sup> From Alfa Inorganics, Inc.

fication gave (49% yield from 1) the dimethyl ester 3: mp 31-31.5° after crystallization from 2:1 ether-pe-



troleum ether ( $\lambda_{max}^{CHCls}$  5.8, 6.06  $\mu$ );  $\lambda_{max}^{EtOH}$  end absorption, shoulders at 245 (log  $\epsilon$  3.19), 265 m $\mu$  (log  $\epsilon$  2.98). The mass spectrum showed m/e 216 (parent), in addition to 185 (base, loss of CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>). The nmr spectrum (CDCl<sub>3</sub>) at 100 Hz showed  $\delta$  2.72 (2 H, a,a' coupled







with c; eight-line ABX pattern), 3.67 (3 H, s, side chain  $CO_2CH_3$ ), 372 (3 H, s, ring  $CO_2CH_3$ ), 3.9 (2 H, b,b' coupled with c and d; ABXY multiplet), 4.65 (1 H, c coupled with a,a', b,b', and d; multiplet), 6.81 (1 H, d coupled with b,b' and c; quartet).<sup>6</sup>

Addition of 3 to excess of butadiene at 180°, with some hydroquinone, gave the crude adduct 4 (pure 4, mp 46.5-47.2° from ether-petroleum ether after glpc on SE 30 at 200°; unexceptional ir and nmr spectra;

(6) For another synthesis of this ester and the oxygen and nitrogen analogs see P. L. Stotter and S. A. Roman, in preparation.

m/e 270 (parent), 196 (base, loss of CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> and H), 137 (loss of CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, H, and CO<sub>2</sub>CH<sub>3</sub>)). Desulfurization (with simultaneous reduction of the double bond) of 4 by refluxing with W-5 Raney nickel<sup>7</sup> in methanol for 18 hr was followed by saponification (40-hr reflux with 20% aqueous ethanolic potassium hydroxide) to yield, in 52% overall yield from 3, the diacid 5, mp 178-179° (lit.<sup>1</sup> mp 179-180°), undepressed on admixture with an authentic sample. The infrared spectra of the diacid 5 and of an authentic sample were identical.<sup>1</sup>

Functionality can also be introduced (cf. B) via substituted butadienes. Addition of 2-ethoxybutadiene<sup>8</sup> (1.5 equiv initially, and 1.5 equiv after 6 hr) to the dihydrothiophene **3** at 185° for 12 hr was followed by dioxolane formation<sup>6</sup> by stirring 1 hr with ethylene glycol in dry tetrahydrofuran (trace of *p*toluenesulfonic acid). Desulfurization, by refluxing with Raney nickel in methanol as above, gave a crude diester which solidified on standing. Recrystallization from ether gave the diester **6**, mp 97-99.5°, in 54% overall yield from **3**. The analytical sample (etherpetroleum ether) had mp 105--105.5° ( $\lambda_{max}^{CHCls}$  5.8  $\mu$ ); nmr (CDCl<sub>3</sub>)  $\delta$  1.15 (~3 H) and 1.65 (~7 H) (overlapping singlet and multiplet), 2.26 (4 H, m), 3.69 (3 H, s), 3.76 (3 H, s), 3.95 (4 H, s).

The expected orientation in the Diels-Alder reaction of ethoxybutadiene and **3**, implied in structure **6**, followed from the mass spectrum of **6** which showed m/e300 (parent), 185 (base), and 99. Identity was further confirmed by converting the keto diacid<sup>10</sup> corresponding to **6** (which was unambiguously synthesized<sup>11</sup> from 7) to its dioxolane dimethyl ester which proved to be identical with our ketal diester **6**.

It is apparent that the new synthesis we have illustrated should be generally applicable to the construction of *cis*-1,2-dialkylcyclohexanecarboxylic acids and to angularly substituted polycyclic systems.<sup>12</sup>



(7) A.A. Pavlick, and Y. Adkins, J. Amer. Chem. Soc., 68, 1471 (1946).

(8) H. B. Dykstra, ibid., 57, 2255 (1935).

(9) Cf. A. J. Birch, J. M. Brown, and G. S. Subba Rao, J. Chem. Soc., 3309 (1964).

(10) W. S. Johnson, D. S. Allen, Jr., R. R. Hindersinn, G. N. Sausen, and R. Pappo, J. Amer. Chem. Soc., 84, 2181 (1962).

(11) For details see P. L. Stotter, Ph.D. Thesis, Columbia University, New York, N. Y., 1968.

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